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# **Innovative Treatment & Remediation Demonstration Program**

**Summary Report:  
Conceptual Model Review and Remediation Options  
for Los Alamos National Laboratory  
Technical Area 54, Material Disposal Area L**

**November 2002**

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**Summary Report:**

**Conceptual Model Review and Remediation Options**  
**for Los Alamos National Laboratory**  
**Technical Area 54, Material Disposal Area L**

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**Abstract**

From June 2001 through September 2002, the Innovative Technology and Remediation Demonstration (ITRD) Program conducted an evaluation of possible remediation technologies at the DOE Los Alamos National Laboratory (LANL) in New Mexico. For ten years (1975 to 1985), LANL disposed of liquid chemical wastes at Material Disposal Area L. Large amounts of the liquid waste have volatilized to create a plume of organic vapor in the subsurface. A Technical Advisory Group (TAG) was formed from the ITRD Program to assess two issues—the conceptual modeling previously performed by LANL Environmental Restoration (ER) and remediation options for the site. The goal of the project was to evaluate a corrective measure strategy proposed by LANL ER, passive venting, with respect to other corrective measures. Although the TAG did not recommend a particular technology, it concluded that, based on LANL's vapor transport modeling, soil vapor extraction is a reasonable remediation method that is likely to be successful. The TAG also provided a more general recommendation: LANL ER and the New Mexico Environment Department should continue to work together to identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at MDA L.

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**ITRD**

LANL TA54 MDA L Technical Advisory Group

One of the purposes of the ITRD program is to provide an independent evaluation of remediation approaches and applicable technologies on a site-specific basis. The "target audience" for ITRD reports includes both the specific site's Technical Advisory Group, which includes DOE site project managers, M&I/O scientists and engineers, regulators, public stakeholders, and technology experts, and also interested parties with similar challenges at other sites throughout the DOE complex. The intent of the program is to provide technical assistance by developing treatment and deployment information on potentially useful innovative technologies, and to make recommendations in conjunction with all of the parties to a remedial action decision. It has been demonstrated that this inclusive process can help build consensus on a site's eventual technology selection and treatment approach.

Because the ITRD process is inclusive and seeks to present information to all interested parties in a fair manner, the *Conceptual Model Review and Remediation Options for Los Alamos National Laboratory Technical Area 54, Material Disposal Area L* Summary Report includes a series of comments and responses in Appendix C between members of the Technical Advisory Group and LANL Environmental Restoration personnel involved with the project.

Several exchanges of comments and responses resulted in no substantial changes to the original Technical Advisory Group findings and recommendations from the draft May 2002 reports, but some text was modified to provide clarification in the context of continued discussion and more recent work. Inclusion of the comments and responses in Appendix C seeks to indicate that there was a diversity of opinion over some issues that was not resolved within the Technical Advisory Group report.

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**Innovative Treatment and Remediation Demonstration (ITRD)  
Summary Report:  
Conceptual Model Review and Remediation Options for  
Los Alamos National Laboratory Technical Area 54, Material Disposal Area L**

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## EXECUTIVE SUMMARY

From June 2001 through September 2002, the Innovative Technology and Remediation Demonstration (ITRD) Program conducted an evaluation of possible remediation technologies at the DOE Los Alamos National Laboratory (LANL) in New Mexico. For ten years (1975 to 1985), LANL disposed of liquid chemical wastes, including uncontained liquid waste and liquid waste contained in drums at Material Disposal Area L (MDA L). Large amounts of the liquid waste, which were disposed of in pits, impoundments, and shafts, have volatilized to create a plume of organic vapor in the subsurface. Testing indicates volatile organic compounds (VOCs) disposed of at this site include 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), trichlorotrifluoroethane (FREON), and lesser amounts of chloroform, toluene, benzene, cyclohexane, methyl chloride, and other similar solvents.

A Technical Advisory Group (TAG) was formed from the ITRD Program to assess two issues—the conceptual modeling previously performed by LANL Environmental Restoration (ER) and remediation options for the site. The goal of the project was to evaluate a corrective measure strategy proposed by LANL ER, passive venting, with respect to other corrective measures. The specific objectives of the TAG were: (1) review the site characterization data and conceptual modeling for the contaminant plume at MDA L, (2) screen remediation technologies to determine those with direct applicability, and (3) identify the most appropriate technology or technologies for remediation of the contaminant plume at MDA L. The criteria used in this evaluation included technical, regulatory, and public acceptability.

Although the TAG did not recommend a particular technology, it concluded that, based on LANL's vapor transport modeling, the proposed soil vapor extraction strategy is a reasonable remediation method that is likely to be successful. However, additional data would significantly improve the understanding of the extent and movement of the subsurface vapor plume. The TAG recommended collection of additional information on vapor flux to the water table and on surface vapor flux. Because a site-specific design has not yet been selected for MDA L, the TAG was unable to evaluate cost-effectiveness, environmental safety and health risk reduction for workers, and safety and risk reduction for the public and the environment.

The TAG also provided a more general recommendation: LANL ER and the New Mexico Environment Department should continue to work together to identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at MDA L. In particular, the following regulatory requirements need to be identified to allow comparison of specific vapor extraction technologies: off-gas emission requirements, process monitoring requirements for soil vapor extraction, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and worker risk levels, and public participation requirements.



## ACRONYMS

DNAPL	dense non-aqueous-phase liquid
DOE	Department of Energy
EPA	Environmental Protection Agency
ER	Environmental Restoration
FREON	trichlorotrifluoroethane
GC	gas chromatography
IR	infrared
ITRD	Innovative Technology and Remediation Demonstration
LANL	Los Alamos National Laboratory
LNAPL	light non-aqueous-phase liquid
LUST	leaking underground storage tank
MDA L	Material Disposal Area L
NMED	New Mexico Environment Department
PESP	Pilot Extraction Study Project
RBCA	risk-based corrective action
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
SVE	soil vapor extraction
TA	Technical Area
TAG	Technical Advisory Group
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
VOC	volatile organic compound

# 1. INTRODUCTION

Based on a request from Los Alamos National Laboratory (LANL), the Innovative Technology and Remediation Demonstration (ITRD) program established a Technical Advisory Group (TAG) to conduct a peer review for a project dealing with remediation options for Material Disposal Area L (MDA L) in Tech Area 54 at LANL. During the second half of 2001, the TAG received background materials provided by the Site Project Manager and briefings from LANL Environmental Restoration (ER) project members. The TAG held its meeting on December 12, 2001, in Pojoaque, New Mexico. At the beginning of the meeting, the TAG was introduced to the ITRD process and the desires of LANL ER and the U.S. Department of Energy (DOE) for an independent peer review. Two subteams of experts were formed to review specific issues: one to review the conceptual modeling previously performed by LANL ER and another to evaluate remediation options for the site. Based on subsequent conference calls and analysis, the TAG prepared this report.

The goal of this project is to assess a corrective measure proposed by LANL ER, passive venting, with respect to other possible corrective measures. The specific objectives are as follows:

1. Review the site characterization data and conceptual modeling for the contaminant plume at MDA L.
2. Screen remediation technologies to determine those with direct applicability to MDA L.
3. Recommend the most viable technology or technologies for remediation of the contaminant plume at MDA L.

The Conceptual Modeling subteam addressed Objective 1. The Remediation Options subteam addressed Objectives 2 and 3. This report combines the work of the two subteams.

Section 2 of this report provides background information on MDA L. Section 3 identifies the criteria that were used to review the conceptual modeling and the remediation options. Sections 4 and 5 summarize the findings and recommendations of the two subteams. Section 6 provides biographical information about the subteam members.

Appendices A and B contain the analyses conducted by the Conceptual Modeling and Remediation Options subteams, respectively, and the results of their evaluations. Appendix C contains comments and responses about issues that were not fully resolved in the TAG report.

## 2. BACKGROUND INFORMATION ON MDA L

Los Alamos National Laboratory is located in Los Alamos County in north-central New Mexico, approximately 97 km (60 mi) north-northeast of Albuquerque and 40 km (25 mi) northwest of Santa Fe (Figure 1). LANL occupies an area of about 112 km<sup>2</sup> (43 mi<sup>2</sup>) located directly south of the town of Los Alamos. LANL is situated on the Pajarito Plateau, which lies between the Jemez Mountains and White Rock Canyon of the Rio Grande River. The Bandelier Tuff, a thick sequence of ash-flow and air-fall pyroclastics, caps the Pajarito Plateau. Erosion of the relatively soft tuff created numerous deep canyons that separate narrow, finger-like mesas. MDA L is a 2.58-acre site on top of Mesita del Buey, within TA-54, that was historically used as a disposal site for laboratory-generated hazardous (non-radioactive) wastes. Land disposal stopped in 1985. It is presently used for RCRA-permitted hazardous waste storage and treatment and for mixed waste storage under interim status authority.



Figure 1. Location of Los Alamos National Laboratory

### 2.1 LANL MDA L PLUME

From 1975 to 1985, LANL disposed of liquid chemical wastes, including uncontained liquid waste and liquid waste contained in drums, in pits, impoundments, and shafts at MDA L. Large amounts of the liquid waste have volatilized to create a plume of organic vapor in the subsurface. Testing indicates volatile organic compounds (VOCs) disposed of at this site include 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), trichlorotrifluoroethane



(FREON), and lesser amounts of chloroform, toluene, benzene, cyclohexane, methyl chloride, and other similar solvents.

## 2.2 MDA L SITE BACKGROUND

Violent eruptions of volcanic ash from the Valles Caldera between 1.2 and 1.6 million years ago deposited tuff layers in the LANL area. Since then, the tuff has eroded to leave a system of alternating finger-shaped mesas and canyons. MDA L is located atop one such mesa, Mesita del Buey, with the waste disposed in shallow pits (4 m or 13 ft deep) and shafts (approximately 20 m or 66 ft deep). The surrounding canyons, Canada del Buey and Pajarito Canyon, lie 30 m (98 ft) below the steep-sided mesa, and the regional aquifer is located approximately 300 m (984 ft) below the disposal pits. The strata immediately below MDA L are composed of nonwelded to moderately welded rhyolitic ash-flow and ash-fall tuffs interbedded with thin pumice beds. The rhyolitic units overlie a thick basalt unit, which in turn overlies a conglomerate formation (Figure 2).

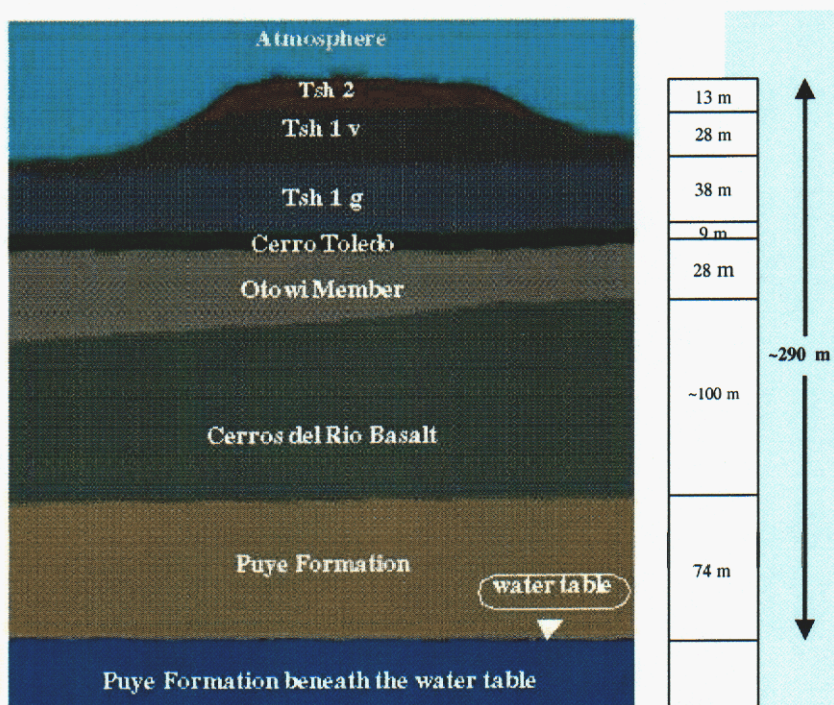


Figure 2. Generalized Cross-Section at Los Alamos National Laboratory

LANL has conducted quarterly sampling at MDA L since 1990, monitoring the pore gas in the VOC plume resulting from the disposal of liquid waste. The pore gas monitoring provided sufficient data for the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) to estimate the nature and extent of the VOC vapor plume at MDA L. Rock samples from boreholes as deep as 92 m (300 feet) indicated no condensed liquid VOC or sorption of organic compounds on the matrix. This observation was consistent with expectations based on the absence of organic carbon, low moisture content, and low specific surface area of the matrix.

As part of the RFI, LANL ER conducted a Pilot Extraction Study Project (PESP) to examine both active and passive vapor extraction with the goal of reducing the size of the VOC vapor plume. LANL gained extensive experience with vapor venting in Bandelier Tuff during the PESP and the RFI investigation at MDA L. During active vapor extraction, the vapor moved at the same velocity as the pore gas, showing no retardation. The absence of retardation was expected due to the absence of condensed liquid VOC. In the PESP, LANL measured both the *in situ* horizontal permeability as a function of depth at several boreholes and the penetration of barometric pressure variations within the Bandelier tuff and the underlying Cerros del Rio basalt. Data analysis shows that, in one stratigraphic unit, vertical gas motion is dominated by fracture flow. LANL also measured the flow in open boreholes that is induced by barometric pressure variations. Close agreement of the data with theory indicates that the flow into and out of a borehole is governed by the horizontal permeability as measured *in situ*, and is reduced by the vertical penetration of barometric pressure variations into the earth from ground surface. Sites with extensive pavement (such as in MDA L) may be slower to respond to atmospheric pressure variations, thereby enhancing the vapor flow in a borehole that is open to the atmosphere.



### **3. PEER REVIEW CRITERIA**

The two subteams developed criteria for reviewing the LANL MDA L conceptual model and the remediation options. Section 3.1 lists the criteria for the conceptual model review; Section 3.2 provides the criteria for the remediation options evaluation.

#### **3.1 CRITERIA FOR CONCEPTUAL MODELING REVIEW**

The TAG assessed LANL ER's conceptual modeling based on the following review criteria:

1. Has the Site Project Team adequately reviewed the pertinent, current technical literature in this area?
2. Are the conclusions cited in their reports supported by the work performed?
3. Have the practical limits of detection been determined in terms of minimum and maximum depth, plume size, and type of contaminant being detected?
4. Do site conditions offer any unique opportunities or constraints in terms of characterization or modeling?
5. Has the Site Project Team collected sufficient data to respond to regulatory, stakeholder, and risk evaluations?
6. Have the technical uncertainties associated with the model been adequately identified and addressed?
7. Does the model adequately represent the field data?

#### **3.2 CRITERIA FOR REMEDIATION OPTIONS ANALYSIS**

The TAG assessed the options for remediation at the site based on the following review criteria:

1. Has the Site Project Team adequately reviewed the pertinent, current technical literature in this area?
2. Is the Site Project Team's proposal for remediation a logical extension of existing technology?
3. Do site conditions offer any unique opportunities or constraints in terms of characterization or remediation?
4. Have the technical uncertainties associated with the application of this technology been adequately identified and addressed?
5. Is there a clear path shown towards measuring the success of the technology?
6. Does this technology show a clear benefit in terms of (a) cost effectiveness, (b) environmental safety and health risk reduction for workers, and (c) safety and risk reduction for the public and the environment?
7. Has the Site Project Team collected sufficient data to respond to regulatory, stakeholder, and risk evaluations?

8. Based on the overall assessment of the site proposal, should it be initiated? If not, what remediation technology should be used and why?

## 4. FINDINGS OF THE PEER REVIEW SUBTEAMS

Sections 4.1 (Conceptual Modeling) and 4.2 (Remediation Options) contain findings of the Peer Review Subteams. Background information for the findings is described in more detail in Appendix A (Overview of the Conceptual Model) and Appendix B (Summary of Remediation Technologies). Some of the findings in Section 4.1 generated considerable discussion between LANL ER and the Conceptual Modeling Subteam. Several exchanges of comments and responses have resulted in no substantial changes to the original TAG findings from the draft May 2002 reports, but some text has been modified to provide clarification of the findings in the context of the continued discussion and more recent work. The comments and responses are included in this report as Appendix C to indicate that there was a diversity of opinion that was not resolved within the TAG report.

### 4.1 CONCEPTUAL MODELING

The conceptual model of the site is by nature a historically inclusive snapshot in time that must evolve as additional accurate information is added to the current site data set. The information that improves the conceptual model is often additional measurements but can also include application of more accurate theoretical behavior of the modeled system or inclusion of results from numerical simulations using the mathematical description of the system dynamics in the numerical model. The conceptual model is the most important construct for characterizing and remediating a contaminated waste site and should be as accurate as possible; however, the development of the conceptual model cannot supersede the primary goal of remediating of the site.

The TAG recognizes that, ultimately, the conceptual model must provide the framework for making correct decisions for the next step on the path to site remediation. If the correct decisions can be made from a scientific basis at a particular time, the conceptual model has served its purpose even though the model may include elements that are not precisely descriptive of the physical behavior of the system. It is important to maintain the perspective of improving the accuracy of the model in the context of cleaning up the site.

The TAG has reviewed the work of the LANL ER project team and agreed with their general conclusions on choices for site remediation and the general conceptual model used to select those choices. The TAG has also identified some areas and made some recommendations for potentially improving the conceptual model of the site.

1. In most areas, the Site Project Team has adequately reviewed the pertinent, current technical literature. The areas lacking are:
  - a. Surface flux including modeling of the boundary layer. The model for the boundary layer is very simplistic and will influence the surface flux of TCA and the plume size. This topic is discussed in more detail as Recommendation 2 in Section 5.1.
  - b. Vapor-solid sorption. Vapor-solid sorption can be important for TCE as experimentally investigated by Ong and Lion (1991) for Bandelier tuff. However, their data indicate that it will only be significant when the moisture content is less than about 1-2%. The minimum *in situ* moisture content is about 2%, with the majority of the units having moisture contents of 10% or greater (Stauffer et al,



2000). Therefore, the TAG does not believe it will play a significant role in this case. However, we recommend that the phenomenon at least be acknowledged and discussed rather than ignored.

- c. In situ degradation. The TAG does not recall any discussion of *in situ* degradation of the plume. Of course, neglecting degradation would be conservative.
  - d. Gas diffusion model. The gas diffusion model is based on Fick's law. For low permeability media, it is well known that Fick's law is inadequate due to the influence of gas-solid interactions and coupling between diffusive and advective effects (Webb, 1998). It is recommended that the permeability of the various units be listed. If the values are greater than  $10^{-13} \text{ m}^2$  ( $1.1 \times 10^{-12} \text{ ft}^2$ ), Fick's law is adequate. If the permeabilities are lower than  $10^{-13} \text{ m}^2$  ( $1.1 \times 10^{-12} \text{ ft}^2$ ), an alternative model such as the Dusty Gas Model should be employed (Webb and Pruess, 2002). The site project team subsequently reviewed the permeability of the sediments and found that the majority of the sediments were greater than  $10^{-13} \text{ m}^2$  ( $1.1 \times 10^{-12} \text{ ft}^2$ ).
  - e. Diffusion coefficient. The diffusion coefficient used in the conceptual model is for gas only; liquid diffusion is neglected. As discussed in Jury et al., 1984a, the effective diffusion coefficient may be influenced by the liquid diffusion value even at low values of moisture content, depending on the value of Henry's constant. The effective diffusion coefficient should be evaluated.
2. The conclusions cited in Site Project Team reports are adequately supported by the work performed.
  3. In some instances, determinations of the practical limits of detection are insufficient. While the best-fit simulation shows that the vapor plume is unlikely to reach the water table, the vertical extent of the plume as illustrated by field data is not presented in the report. Two issues are of concern:
    - The New Mexico Environment Department (NMED), the U.S. Environmental Protection Agency (EPA) Region 6, and the public may require site-specific data before they accept that the vapor plume has not and will not reach the water table; and
    - While the imposition of a zero concentration condition appears justified, its exact location as determined by field data or a comparison of modeling results to field data is not known.

Installation of deeper wells capable of providing concentration data at the bottom of the plume is recommended. Data from such wells will directly address the first concern and can also be used to refine the modeling of transport processes at the bottom of the plume.

At the time the report was written, no core sample measurements were available for the Cerros del Rio Basalts (Figure 2). Therefore, the numerical model was formulated using a surrogate porosity and a modeled saturation value. Further refinements to the numerical simulations can be realized if property measurements can be made on the basalts via the deep wells.

4. Site conditions offer some unique features in terms of characterization and modeling. Some of the units are known to have fractures, yet the conceptual model developed by Stauffer et al., 2000, is a porous media approach without fractures. Because many of the

fractures are vertical, they would enhance the vertical migration of the plume and could conceivably increase the calculated migration of the plume.

5. LANL ER has collected a considerable amount of site characterization data, much of it directly related to constructing the site conceptual model, responding to anticipated regulatory and stakeholder concerns, and understanding risks associated with site remediation. However, LANL ER should be aware that, in at least a couple of situations, the data may be considered insufficient by regulators and stakeholders. For example, the depth of the plume is not adequately defined, and the predicted surface flux of the contaminants seems inconsistent with the data.
6. Many of the technical uncertainties associated with the model have been adequately identified and addressed. The diffusion model was selected for this site after analysis of the available site characterization data and in consideration of the magnitude of the plume, the objectives of the model (determine a remediation strategy and predict gross behavior of the plume), and the complexity of the geology. In general the model seems to predict the current characterization data set. There are, however, some technical uncertainties that need to be addressed, such as the boundary layer modeling and the effect of fractures on plume growth or dissipation, and contaminant transport.

The conceptual model described in (Stauffer et al., 2000) does not provide sufficient background information regarding

- a. Surface flux predictions. The surface flux predictions by the model are based on two assumptions that need to be further justified.

The first one is the thickness of the boundary layer. The model assumes this to be 1 m (39 in) thick: What is the basis for this assumption?

The second one is the overall mass transfer coefficient or diffusion coefficient used in this calculation.

- b. Treatment of fractures. It has been reported that some of the geological units at the MDA L are vertically fractured, which can enhance the release of the vapors. The manner in which fractures are included in the conceptual model needs to be described in more detail or evaluated further.
7. The model seems to give reasonable answers compared to the field data. However, some of the details are insufficiently explained, and some additional data or modeling studies are needed. Appendices to the Stauffer report (Stauffer et al., 2000) of the available concentration data would be useful. The current model can be used to select and implement some remediation field tests and develop general strategies for contaminant control and remediation. The current model can also be used to focus the next set of characterization data needs and identify areas for more refined numerical modeling.

## **4.2 REMEDIATION OPTIONS**

1. The subteam believes the Site Project Team has adequately reviewed the pertinent, current technical literature in the area. Given the conceptual model based on the characterization data to date, they have reviewed the available remedial alternatives and have focused on strategies that are likely to be successful. These are generally technologies based on either active or passive soil vapor extraction (SVE).



2. The Site Project Team's proposal for remediation is a logical extension of existing technology. However, specific aspects of the technology and the configuration of the cleanup have not been determined. There are techniques within SVE that could be used, but these are yet to be determined.
3. Site conditions at MDA L offer unique opportunities in terms of characterization and remediation. Site characterization data indicate that air is found in the formation below the mesa and flows upward. This effect produces a zero-boundary condition for contaminant concentrations. LANL has already used these characteristics in their modeling, but they may also be able to capitalize on this condition for cleanup opportunities.
4. LANL ER has addressed some of the technical uncertainties associated with the application of this technology. Soil vapor extraction is commercially available and appropriate for this application, and it is the presumptive cleanup remedy of the EPA. However, the Site Project Team has not yet provided a formal proposal for the technology design. Soil vapor extraction has been tried in various modes and it will work, but the exact configuration for MDA L has not been determined. Some of the specific aspects of SVE that must be considered are
  - Passive/active venting
  - Off-gas treatment
  - Surface flux
  - Type of mass removal to be achieved
  - Location (impact on site operations)
  - Risk assessment
  - Specific design parameters
5. The subteam believes that LANL ER will be unable to measure the success of the technology until the regulator and the site reach consensus on clear performance metrics. LANL ER undertook this project even though quarterly monitoring and sampling indicate the vapor plume at MDA L poses no current threat to either human health or the environment. LANL ER and the NMED need to work together to identify the regulatory requirements that will guide the process. One possibility is a risk-based corrective action (RBCA) study showing the remaining contaminant sources are below some threshold after the bulk of the contaminants have been removed.
6. The technology was examined to evaluate benefits in terms of (a) cost effectiveness and (b) environmental safety and health risk reduction for workers and safety and risk reduction for the public and the environment:
  - The technology screening performed by this subteam (see Appendix A) indicates that SVE is generally a cost-effective cleanup remedy. However, for application to MDA L, the overall cost will depend on the technology design, which has not yet been determined for MDA L.

- Soil vapor extraction has been used safely and successfully in many different applications. However, for application to MDA L, the overall safety and risk will depend on the technology design. Some general comparisons to alternatives may provide insight into general risks, such as comparisons to excavating the source and comparisons between active and passive systems with respect to disruptions in site operations. Risk and safety may also depend on choices of system components, such as the strategy for off-gas treatment.
7. The Site Project Team has collected sufficient data to adequately support most of its conceptual modeling assumptions and its proposal for remediation. However, additional data collection for a few parameters could strengthen the site's case for using SVE. For example, additional data could be collected for
    - Flux to the water table (also an NMED concern)
    - Surface flux to the atmosphere
  8. Based on site characterization data and modeling for the site, the subteam believes the Site Project Team proposal to use SVE at MDA L should be initiated. However, the subteam can give only a qualified endorsement until it has an opportunity to examine the site-specific design for MDA L.

## 5. RECOMMENDATIONS

Sections 5.1 (Conceptual Modeling) and 5.2 (Remediation Options) contain the recommendations of the Peer Review Subteams. Some of the recommendations in Section 5.1 generated considerable discussion between LANL ER and the Conceptual Modeling Subteam. Several exchanges of comments and responses have resulted in no substantial changes to the original TAG recommendations from the draft May 2002 reports, but some text has been modified to provide clarification of the recommendations in the context of the continued discussion and more recent work. The comments and responses are included in this report as Appendix C to indicate that there was a diversity of opinion that was not resolved within the TAG report.

### 5.1 CONCEPTUAL MODELING

Based on a careful assessment of the information presented to the TAG and the findings developed in response to the review criteria, the Peer Review Subteam provides the following recommendations:

1. Surface emission measurements. The TAG has agreed that the quarterly monitoring at TA 54 MDA L can be relaxed. However, the TAG recommends that additional surface flux measurements be made, preferably by perforating the impermeable cap at some locations. The rationale for this recommendation is as follows:

It is being proposed by the Remediation Sub-committee of TAG to use the conceptual model in evaluating and designing remediation alternatives. Before the model can be used for this purpose, it needs to be further validated. Previous validations have compared measured subsurface vapor phase concentrations and surface emissions against model predictions.

While the agreement between measured and predicted subsurface concentrations were reasonable, there were notable differences between the corresponding surface fluxes. By perforating the cap, two "data points" can be obtained to further calibrate and/or validate the conceptual model: sampling of the gas phase concentration as well as measurement of the flux.

In response to the original TAG report on the conceptual model (Appendix A to this report), Don Neeper of LANL suggested that CO<sub>2</sub> measurements could be correlated to VOC emissions due to barometric pumping. This is a reasonable approach; however, the correlation between CO<sub>2</sub> emissions and VOC emissions has to be first demonstrated.

A further benefit of surface flux measurements will be in risk evaluation that is being recommended by the two subteams of the TAG.

The parameters used in the model to predict the surface emissions (viz. the boundary layer thickness and the diffusion coefficient) need to be re-evaluated (see Recommendation 2 below).

2. Surface flux. The size of the contaminant plume, including whether or not the plume continues to grow or shrink, is based on a balance between the estimated source of the



contaminants and the loss to the atmosphere, or the surface flux. Therefore, the surface flux is a significant factor in the long-term behavior of the plume.

The modeled surface flux is based on a porous media diffusion coefficient and a 1-m (39-in) transition to a zero concentration in the atmosphere, or boundary layer. This approach is extremely simplified. A more accurate representation of the boundary layer thickness is suggested by Jury et al. (1984b) to be typically 0.5 cm (0.2 in), although values can range up to 1 m (39 in) for very low wind speeds and stable conditions (Webb et al., 1999). The diffusion coefficient should also be that for open conditions, not for a porous media, which would tend to increase flux to the atmosphere.

Surface flux measurements that were made at x discrete points showed much lower flux (up to 300 times less) than indicated by the model. The discrepancy raises concern with the accuracy of the model. However, these measurements were not made according to standard methods for quantitative flux measurement and were made at a limited number of locations. Given the natural and anthropogenic heterogeneities of the surface and shallow subsurface, it is likely that these small numbers of flux measurements are not representative of an average flux over the waste site area. They are therefore of limited value in model validation. Further model runs were completed using reduced surface flux values (similar to those measured), which provided dramatically different plume shape and extent results that conflicted with subsurface gas concentration measurements. Given the larger data set and higher accuracy of the subsurface concentration measurements, it is important that the model faithfully simulate these data. Nevertheless, since the growth of the plume is significantly affected by the value of surface flux, efforts should be made to devise a strategy for quantifying this parameter.

To more closely represent the dynamics of the surface/subsurface processes, it is recommended that the model be modified in the future to correct boundary behavior and that additional quantitative flux measurements eventually be made to reconcile and verify the model. These recommendations would be appropriately implemented to support work on the selection of remedial alternatives.

3. Presence of Fractures. Some of the units are known to have fractures, yet the conceptual model developed by Stauffer et al., 2000, is a porous media approach without fractures. This approach may be justified if the fractures are filled with porous media. However, if the fractures are of a higher permeability than the bulk formation and because many of the fractures are vertical, they could enhance downward vertical migration of the plume or increase flux of the contaminant out through the surface.

Apparently vertical fractures are mainly found in the welded section of TSH Unit 2 and much less commonly below; therefore these fractures may not impose a significant additional plume migration risk. However, it is recommended that the effect of fractures on plume migration and potential remedial strategies be investigated when evaluating the selection of remedial alternatives.

4. Alternative Methods for Gas Sampling and Analysis at MDA L Site. The TAG recommends continuing to acquire more concentration data at the site using inexpensive but accurate field screening or simple laboratory techniques to support the selection of remedial alternatives as well as to evaluate the effectiveness of the performance of the remediation technique.

To obtain a more accurate conceptual model of the subsurface contamination at the MDA L site, more soil gas measurements are required. Current protocol calls for analysis using Summa Canister collection and contract lab analysis by EPA protocol. This procedure is expensive and not well suited for obtaining a better conceptual understanding of the gas plume at the site. To understand the dynamic behavior that is characteristic of subsurface contaminant gas phase plumes, many inexpensive measurements would be most useful. There are a variety of field and local laboratory (i.e., on site or mobile lab) gas sampling and analysis methods available for deployment. These methods range from standard laboratory methods brought to the field (e.g., gas chromatography/mass spectrometry) to simple detectors sensitive primarily, but not exclusively, to the species of interest (e.g., photoionization detectors, portable acoustic wave sensors, chemiresistors, etc.). Any of these methods may be appropriate depending on the analytes in the gas stream, the detection levels required, the frequency of measurement, etc.

LANL site personnel have been using a method that falls between these types of sensors (Innova Model 1312 infrared photoacoustic spectrometer). This instrument is species selective based on the infrared absorption spectrum of the target analyte(s). The instrument is capable of simultaneously and accurately measuring concentrations of 5 different species so long as their infrared spectra have no significant overlaps. The instrument is capable of detecting gas concentrations of the species of interest (volatile chlorinated organic compounds) to approximately 1 ppmv and can cover a dynamic range that approaches the vapor pressure limits of many of the compounds. It is also capable of semi-continuous monitoring (every 1 to 4 minutes) and unattended field deployment. Comparisons of the instrument with the baseline gas chromatography (GC) methods show that the Model 1312 is at least as stable, repeatable, and accurate as GC. One significant issue that may affect the selection of this technology for gas sampling and analysis at a site is the error introduced by analytes with interfering infrared (IR) spectra. Even low concentrations of some compounds with rich IR absorption spectra may affect accurate analyses of species with nearby IR peaks. Some of the freon compounds (Freon 11, 12, and 113) have particularly rich IR spectra and can interfere with measurements of PCE, TCE, and TCA. Freons have been detected at MDA L, and the site has performed measurements comparing results from the B&K Model 1312 and baseline Summa canister gas chromatography. The comparisons show a strong correlation between the two analytical methods for the contaminants of concern (TCA and TCE). The B&K model 1312 is therefore a satisfactory technique for tracking plume behavior.

Other gas analysis technologies may also be suitable for the characterization and monitoring needs of the site and should be evaluated on the basis of the data objectives of the owners, regulators, and other stakeholders of the site.

Some percentage of split samples should be sent for analysis by the baseline method to ensure the analysis performed using an alternative technique to the baseline protocol is an adequate representation. Often, the ratio of alternative method to baseline analyses is 90:10. For the MDA L, the ratio of alternative method samples to baseline may be more or less depending on the performance of the method, the characteristics of the gas sample, the number of samples needed and other issues decided by a consensus of the site and regulators.



## **5.2 REMEDIATION OPTIONS**

Based on a careful assessment of the information presented to the TAG and the findings developed in response to the review criteria, the Peer Review Subteam provides the following eight recommendations. The supporting details for the recommendations are included in Appendix B.

### **Site Hydrogeologic Conditions and Contaminant Distribution**

1. Identify a small number of extraction well configurations, perhaps three alternatives each for an active system and three for an atmospheric pumping system, and use the model to evaluate contaminant removal from the subsurface environment for each of these alternatives.
2. Due to the large body of knowledge that has already been collected (as discussed in Appendix B), additional pump testing of vapor extraction wells is not needed at this site.

### **Characterization of the Source Term**

3. Perform a corrective measures study to determine the feasibility of removing the waste materials from the disposal shafts or stabilize them in place.
4. The remedial system design should include consideration of future drum burst events and provide assurance that contaminant release does not pose an excessive risk to human health and the environment.

### **Nature of Site Operational Activities**

5. Technical Area (TA)-54 site managers should be contacted and asked to identify facility operations that might be impacted by an SVE system. A map of the site should be prepared which delineates structures or areas that cannot have wells, piping or SVE equipment located near them. Areas where site personnel spend large amounts time should also be identified so that the system design can minimize work place hazards.
6. Once a preferred SVE option has been determined, TA-54 site managers should review the plan and the construction phasing to be sure that its impact on site operations will be acceptable. As construction progresses, this coordination should be maintained.

### **Regulatory Constraints**

7. LANL and NMED should continue to work together and identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at TA-54. In particular, the following information must be identified: off-gas emission requirements, SVE process monitoring requirements, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and work risk levels, and public participation requirements.

### **Cost**

8. LANL should conduct a design study that includes variations of the SVE remediation process—specifically, the use of active, passive, and combinations of the two vapor

extraction methods along with active or passive soil gas flushing (clean air or other). Each design should incorporate all of the components needed to comply with regulatory requirements including off-gas emission treatment as needed. The length of time needed to achieve site remediation or achieve the consensus environmental goals (e.g., limit flux to the receptors) should be determined for each. The annualized and total costs of each alternative and the benefit with respect to the goals should be determined and used in selection of a final remediation process.

## 6. BIOGRAPHICAL SUMMARIES OF THE MEMBERS OF THE PEER REVIEW SUBTEAMS

**N. Nirmala Khandan (Subteam Chair) [NMSU]** - N. Nirmala Khandan, Ph.D., P.E., is a Professor of Environmental Engineering at the New Mexico State University in Las Cruces, NM. He received his undergraduate degree in mechanical engineering from the University of Ceylon, Sri Lanka and his graduate degrees (M.S. & Ph.D.) in environmental engineering from Drexel University, Philadelphia, PA. Dr. Khandan has had over ten years of turnkey engineering experience in system designs, project implementation, R&D services in water supply and treatment and has had consulting appointments with over twenty-five U.S. industrial, chemical municipal, biotechnical, environmental, and consulting companies. He has also served internationally – training, presenting papers, giving workshop/short-course presentations, and demonstrating pilot research projects throughout the world. Dr. Khandan has co-written over fifty journal articles and twenty-six-conference proceedings. Amongst the many awards and recognitions that he has received are the following: Founders Award for the Outstanding Research Paper published in Water Research (1991), Instructor, General Motors Distance Education Program (1998) and El Paso Natural Gas Foundation Faculty Achievement Award (1996); and Bromilow Award for Outstanding Research (2001) at New Mexico State University.

**John Kupar [TechCon]** - John M. Kupar (B.S., Geology and Economics, Syracuse University, June 1979) has over 17 years of experience in international and domestic environmental project implementation with emphasis on technical management and project development. Several of the technologies he has successfully deployed include; *in situ* and *ex situ* chemical fixation, thermal desorption, groundwater treatment, wetlands treatment, and dredging. His current interests include the characterization and remediation of contaminated sediments. Since 2000, he has served as a staff member of Argonne National Laboratory's Environmental Assessment Division where he supports the Department of Energy's TechCon program. In this role, he provides technical assistance to DOE environmental restoration project teams in the identification and selection of environmental technologies. Mr. Kupar is a registered Professional Geologist in the Commonwealth of Pennsylvania.

**Joe Rossabi [SRTC]** - Joe Rossabi is a fellow engineer in the Environmental Sciences and Technology Division of the Savannah River Technology Center where he performs applied research and development of environmental characterization and remediation technologies and strategies. His research involves field-testing and implementation of cone penetrometer-based characterization and remediation methods, multiphase flow processes including dense non-aqueous phase liquid (DNAPL) fate and transport, and passive methods for characterization and remediation of subsurface contaminants. Dr. Rossabi was part of a team that deployed a cone penetrometer-based spectral gamma probe to characterize the Cesium plume at the R Reactor Seepage Basin site at SRS. He was also the principal investigator of Department of Energy projects that successfully developed innovative DNAPL characterization methods and implemented barometric pumping for subsurface characterization and remediation of volatile contaminants. Rossabi has numerous publications on subsurface characterization and remediation and has served on national



committees (DOE and EPA) to review characterization and sensing technologies. Before coming to the Savannah River Technology Center eleven years ago, Rossabi performed research and development in the areas of laser communications and atmospheric transmission and spectroscopy for Bell Laboratories in Holmdel, NJ, and a defense contractor in McLean, VA. He has a Ph.D. in Environmental Engineering from Clemson University, an MS in Environmental Engineering from the University of North Carolina at Chapel Hill, and MS and BA degrees in Physics from the State University of New York at Binghamton.

**Malcolm Siegel [SNL]** - Dr. Malcolm D. Siegel (BA, Chemistry, Columbia University; MA, Ph.D., Geological Sciences, Harvard University) is the Technical Coordinator of the Innovative Treatment Remediation Demonstration program and a Principal Member of the Technical Staff at Sandia National Laboratories. He has had over 21 years of research and project management experience involving geochemical laboratory studies, reactive transport simulations, and performance assessment calculations in support of the Waste Isolation Pilot Plant program, the proposed Yucca Mountain high level nuclear waste repository, design of reactive treatment zones and studies of natural attenuation. He is the author of over 45 scientific articles, chapters and peer-reviewed reports.

**Mike Smith [TechLaw, Inc.]** - As an environmental engineer and researcher, Mr. Smith possesses 21 years of experience in the analysis and modeling of transport processes, the assessment of human health and environmental risks, and the collection and analysis of worker health and safety information. For the past eleven years, Mr. Smith has performed analyses related to human health and ecological risk assessments ranging from the dispersion and deposition of constituents emitted from open burn/open detonation processes to the impact of hazardous constituents on indoor air quality. He has reviewed a variety of multi-media/multi-pathway risk analyses submitted to EPA under RCRA and CERCLA. He has conducted permit reviews and analyses and presented training information in support of EPA's RCRA program. Current areas of concentration include dispersion modeling of air emissions and the assessment of human health and environmental risks for hazardous waste combustion units.

**Bruce Thomson (Subteam Chair) [UNM]** - Bruce Thomson is a Professor in the Department of Civil Engineering at the University of New Mexico. He has a B.S. degree in Civil Engineering from the University of California at Davis, and M.S. and Ph.D. degrees in Environmental Science and Engineering from Rice University, Houston, TX. He is a registered Professional Engineer in the State of New Mexico. His research interests focus on the chemical behavior and treatment of radioactive and inorganic water contaminants in both surface and ground water systems. He has worked on remediation of contamination from uranium mining and milling activities, biological transformation of arsenic and other metals, development of treatment technologies for arsenic removal, evaluation of point-of-use treatment systems, and estimation of the costs of treatment. He was a member of the National Research Council's Committee on Mixed Waste and is currently a member of the NM Mining Commission, the City of Albuquerque Technical Standards Comm

**Steve Webb [SNL]** - Stephen W. Webb is from Sandia National Laboratories in Albuquerque, New Mexico. He is a Principal Member of the Technical Staff in the Environmental Technology Department and received his Ph.D. in Mechanical Engineering from Lehigh University where he specialized in heat transfer and fluid flow modeling and analysis. He has performed fluid flow and heat transfer research in such varied fields as



nuclear reactor accident analysis, gas flow in porous media, the effect of weather boundary conditions on transport in soil, explosive chemical movement in soil, natural convection in underground caverns and repositories, and plume dispersion in the atmosphere. He has over 75 publications including journal articles and conference proceedings.

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# **APPENDIX A: OVERVIEW OF THE CONCEPTUAL MODEL**

## **OF SUBSURFACE VAPOR-PHASE PLUMES AT TA54- MDA L AT LANL**

ITRD Conceptual Modeling Subteam  
Dr. Nirmala Khandan, Chair

### **Executive Summary**

Evaluation of the alternatives for restoration of the Material Disposal Area L, (MDA- L) in Technical Area 54 (TA54) is an Innovative Treatment and Remediation Demonstration (ITRD) project at Los Alamos National laboratory (LANL). The major concern at this site has been identified to be organic solvent vapors in the subsurface resulting from disposal of mixed liquid wastes during 1975 -1985. Under LANL's Environmental Restoration Project, extensive sampling and pilot extraction studies have been undertaken at this site to-date; a conceptual model to characterize the subsurface plume has also been developed.

In mid-2001, a Technical Advisory Group (TAG) was formed by ITRD to provide technical assistance in the selection of remedial actions for MDA L. The specific goals of the TAG are to evaluate the site and assess passive and active venting versus other applicable technologies to remediate the site. The first meeting of TAG was held in Dec 2001. The objectives of this meeting were to provide background information on the project to TAG members; to review the conceptual model; and to identify innovative technologies that could be adapted at MDA L.

This report is a follow-up to the TAG's first meeting, documenting the discussions relating to the conceptual model developed by LANL's Environmental Restoration Project Group. Included in this report are: the background to the contamination at MDA- L TA 54 as it relates to the conceptual model; the reasons for developing the model; the simplifying assumptions behind the model; the modeling approach; model simulation results; and conclusions and suggestions.

### **Background**

The MDA L facility has been receiving hazardous and radioactive liquid wastes from the late 1950s until its closure in 1986. Up to 1975, the materials were disposed of in bulk liquid form in open pits, allowing high vapor pressure constituents to evaporate into the atmosphere. From 1975 onwards, organic liquids were disposed of in a series of 20-m (65-ft) deep shafts, ranging in diameters from 1 m to 2 m (3 ft to 6 ft). The bottom of these shafts were ~300 m (~980 ft) above the regional aquifer. These shafts received organic liquids in free liquid form as well as in containerized form. Upon closure, most of the 2.5 acres of the site were covered with asphalt.

Based on the analysis of core samples and pore gases at the site, the following conclusions have been made:

- 34 disposal shafts are the Potential Release Sites (PRS) at MDA L;

- free organic liquid is not found below the shafts;
- sorbed organics are not found below the shafts;
- pore gases are contaminated with volatile organic compounds (VOCs);
- the VOC vapor plume has migrated over 100 m (330 ft) laterally from the shafts;
- the total mass of VOCs in the plume is approximately 1000 kg (2200 lbs);
- the primary constituents of the plume are 1,1,1-trichloroethane (75%); trichloroethene (12.5%); and Freon (11%).

The conceptual model was built upon the above conclusions; hence the validity of the conceptual model is highly dependent upon these conclusions.

### **Reasons for Modeling**

A mathematical model of MDA L at TA 54 may be a valuable tool for one or more of the following functions:

- to analyze the current state of the plume
- to evaluate sensitivity of characteristics of the medium and/or contaminants
- to predict the state of the plume in the future
- to predict surface fluxes and emissions
- to optimize sampling and monitoring
- to evaluate impacts of catastrophic releases
- to evaluate the effectiveness of alternate remediation technologies

Mathematical models are approximations of the real world. They are constructed based on (1) simplifying assumptions; (2) understanding of the processes involved; and (3) the characteristics of the medium and the contaminants. It is, therefore, prudent to make appropriate and valid assumptions in developing the model. It is also necessary to calibrate and validate the model using past data from the site to justify the assumptions, so that the model can be used confidently for predictive purposes.

### **Assumptions in Modeling**

Based on historic data as well as pore gas and core sampling data obtained at site, the following simplifying assumptions have been made in developing the conceptual model for MDA L at TA 54:

- Infiltration is negligible and the subsurface is therefore unsaturated.
- Since 75% of the plume averaged over 140 sampling locations is 1,1,1-trichloroethane (TCA), it is chosen as the target contaminant.
- Since the maximum observed concentration of TCA (~ 3,400 ppmv) is almost two orders of magnitude less than its vapor pressure (~150,000 ppmv), and 170 core samples from



18 boreholes did not reveal any liquid form, no free liquid form of VOCs is present anywhere within the model boundaries.

- Barometric pumping is included in the model as enhanced diffusion, with no air flow through the bulk soil medium.
- Since no air flows through the bulk soil medium, transport of the VOC vapors within the model boundaries is by diffusion only and not by advection.
- The contaminants are nonreactive (as demonstrated in a study at UNM).

## Modeling Approach

The conceptual model for MDA L at TA 54 is a 3-D finite element formulation based on conservation of mass. Following the assumptions listed above, the general advective-diffusive transport equations reduce to a diffusion equation in this case. The model requires inputs for soil and contaminant characteristics; contaminant sources; and numerical discretization and appropriate boundary conditions.

### *Soil and contaminant characteristics:*

The subsurface at the site has been simplified into seven stratigraphic units. The primary hydrogeologic properties relevant to the conceptual model are the porosity and the saturation; the transport property is the diffusion coefficient. The values used in the model are tabulated below.

Unit	Thickness [m]	In situ Saturation [-]	Effective Porosity [-]	Effective Diffusion Coefficient [10 <sup>-6</sup> m <sup>2</sup> /s]
Unit 2	13	0.05	0.48	4
Unit 1v	28	0.04	0.51	4
Unit 1g	38	0.2	0.48	4
Cerro	9	0.3	0.473	4
Otowi	28	0.25	0.435	4
Cerros del Rio Basalts	104	0.25	0.23	4
Puye Formation	74	0.25	0.25	4

The shafts, asphalt cover, and the uncovered surfaces are modeled with the following base characteristics:

Unit	Effective Porosity [-]	In situ Saturation [-]	Effective Diffusion Coefficient [m <sup>2</sup> /s]
Shafts	0.5	0.05	4.0E-06
Asphalt Cover	0.5	0.05	1.0E-14
Uncovered Surfaces	0.48	0.05	4.0E-06

The porosity and saturation values for the Puye Formation are estimated. Corresponding values for the basalt are from similar soils studied elsewhere. All other hydrogeologic data had been measured at site from core samples. Diffusion coefficient for TCA vapor measured on core samples of Bandelier Tuff at TA 54 is used for all the units. A value for the diffusion coefficient in asphalt was assumed.

To evaluate the reliability of the above data, sensitivity analyses were conducted by running the model at various values around the above base values. The model results were relatively insensitive to the properties of the Puye Formation and the basalt.

#### *Contaminant sources:*

Based on historic data, one pit, three surface impoundments, and 34 disposal shafts had been in use at MDA L for varying purposes over varying periods of time. Out of these, the surface pit and impoundments had not received any organic liquids; the 34 shafts are known to have received organic liquids, in pure liquid form as well as in containerized form. Hence, only the shafts are included in the model as contaminant sources. Shafts 1 through 28 were in operation from 1975 through 1985; shafts 29 to 34 were in operation from 1983 through 1985.

In the model, organic liquids are assumed to leak slowly from the containers (55-gal drums) and volatilize immediately. The migration of the vapors through the subsurface is modeled as a time-release phenomenon. Because of the coarse node spacing in the model, each shaft is not identified as an individual source; rather, they are grouped into two clusters: cluster #1 with shafts 1 through 28, and cluster # 2 with shafts 29 through 34.

Typical model simulations begin in 1975 with a constant TCA concentration of 3,000 ppmv in cluster # 1; the simulation is then paused in 1983, and cluster # 2 is added, with a constant TCA concentration of 3,000 ppmv; simulations are then continued till 1985, at which point the asphalt cover is added to the model by changing the diffusion coefficient at the surface.

#### *Numerical discretization and boundary conditions:*

The model domain is rectangular in plan view, 411 m (1350 ft) in the east-west direction and 290 m (950 ft) in the north-south direction. Vertically, the model domain extends from the land surface to below the water table. The top surface is modeled after the topography of the site while the bottom surface is horizontal. The volume of model domain is  $43 \times 10^6 \text{ m}^3$  ( $1.5 \times 10^9 \text{ ft}^3$ ). The node spacing is set at 15.24 m (50 ft) in both horizontal directions; in the vertical direction, it varies from 1 m to 15.24 m (3 ft to 50 ft). These spacings were chosen to achieve a reasonable computation time, with a total of 25,456 nodes and 147,438 tetrahedral elements.

At the top boundary, the atmosphere is fixed at a constant temperature of 10°C (50°F) and a pressure of 0.078 Mpa (1630 lb/ft<sup>2</sup>). The TCA concentration at the nodes above the surface is fixed at zero. The bottom boundary is set as a no flow boundary, at a constant temperature of 25°C (77°F). The vertical side boundaries are set as no flow boundaries.



## Model Simulation Results

The conceptual model has been run under various conditions for calibration, validation, and sensitivity analyses. Model results have been compared against observed data in terms of TCA concentrations and surface fluxes.

### *TCA concentrations:*

Following accepted practice, a modified percentage error and an outlier deletion algorithm have been proposed to demonstrate the goodness of fit between the predicted and observed TCA concentrations. Measured data from the second quarter of FY 99 were used to compare against the model predictions. After deleting 29 data points from a total of 142, a reasonable agreement ( $R = 0.84$ ) was found between measured data and the model predictions with baseline input data.

The best fit between simulation results and measured data was found for the following conditions: zero TCA concentration along the north and west boundaries, and the basalt unit at all times. When compared on the basis of amount of TCA in the subsurface as a function of time, the results predicted with base line data indicate that the system will take longer than the best fit simulation to reach steady state. Also, it will result in a larger mass of TCA in the subsurface. This result is as expected because of the zero-concentration boundary conditions imposed for the best fit simulations.

### *Surface flux:*

Surface concentrations predicted by the base line model were used to estimate surface flux assuming a  $D$  value of  $4 \times 10^{-6} \text{ m}^2/\text{s}$  ( $4.3 \times 10^{-5} \text{ ft}^2/\text{s}$ ) and a transition zone of 1 m (39 in) thick. The predicted flux was about 300 times greater than the measured flux ( $0.1 \text{ kg/m}^2 \text{ yr}$  vs.  $0.00034 \text{ kg/m}^2 \text{ yr}$  [ $0.02 \text{ lb/ft}^2 \text{ yr}$  vs.  $0.00007 \text{ lb/ft}^2 \text{ yr}$ ]). A simple estimate of the flux assuming a TCA concentration of 1000 ppmv, however, results in a flux of  $0.144 \text{ kg/m}^2 \text{ yr}$  ( $0.03 \text{ lb/ft}^2 \text{ yr}$ ) with the same  $D$  value. This anomaly has been ascribed to rain fall during the sampling period.

## Conclusions and Suggestions

The TCA concentrations predicted by the model are in reasonable agreement with the measured data. Thus, the basic assumptions upon which the model has been constructed, as well as the boundary conditions and the model inputs seem to be appropriate for MDA L at TA 54. Consequently, the model can be used with confidence for predicting future state of the TCA plume as well as the effectiveness of any remedial actions.

The best fit model indicates that the plume is currently reaching near steady state conditions, implying that the mass of TCA released by the sources is balanced by the atmospheric emissions. This condition is expected to last until 2060, when all the liquid TCA will be depleted; thereafter, the plume will begin to shrink. Based on this prediction, subsurface sampling frequency may be reduced.

The development of a statistical technique to demonstrate that the plume is not growing is recommended. Ways to estimate mass of TCA in the plume using the measured data are also recommended. In addition, monitoring of emissions, instead of subsurface sampling, may be beneficial in further validating the model.



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## **APPENDIX B: SUMMARY OF REMEDIATION TECHNOLOGIES**

### **DEVELOPED FOR HALOGENATED VOLATILE ORGANIC COMPOUNDS AT LANL TECHNICAL AREA 54**

ITRD Remediation Subteam  
Dr. Bruce Thomson, Chair

#### **Introduction**

Los Alamos National Laboratory (LANL) has developed a proposed process for remediating volatile organic compound (VOC) contamination from unsaturated formations at Technical Area (TA) 54, Material Disposal Area (MDA) L. The contaminants of concern principally consist of chlorinated solvents including tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA) and vinyl chloride (VC). Lesser amounts of other solvents, freons and other contaminants were also disposed at this site (LANL, 2001a). The contaminated formations are primarily unsaturated soils and volcanic tuff in which the contaminants are believed to be present in the vapor phase and adsorbed to soil materials; no phase separated liquid is believed to be present. Four sites within TA 54 are contaminated. Details of the site geology, hydrology, and extent of contamination were presented at a meeting on 12/12/01 of the Innovative Treatment and Remediation Demonstration (ITRD) project team. Additional information has been summarized on a CD-ROM prepared by LANL (2001b).

The remediation strategies proposed by LANL focus on passive and active extraction of subsurface soil gas. Much work has been conducted to model vapor phase transport at this site to support this strategy (Stauffer, et al. 2000). In addition, some field scale pilot testing has been performed to develop preliminary estimates of the performance of potential vapor extraction alternatives (Neeper, 2001).

One of the objectives of the ITRD process is to evaluate innovative technologies in the context of existing and more established remediation methods. Significant experience has been gained over the past 15 years in remediation of soil and ground water contamination from chlorinated aliphatic hydrocarbons (CAH or halogenated VOCs) such as those present at TA-54 MDA-L. The objective of this paper is to identify other options that have been used for remediating unsaturated soils contaminated with halogenated VOCs and briefly to consider their applicability at LANL.

#### **Methods**

It is beyond the scope of the ITRD program or this evaluation to provide a review of all candidate technologies that might have application at LANL. Instead, the Technical Advisory Group (TAG) used a remediation technologies screening matrix that was originally developed by the U.S. Environmental Protection Agency (EPA) and U.S. Air Force in 1993 (US EPA, 1993) and has subsequently been updated and revised twice. The most recent version (Van Deuren et al, 1997) was revised by the Federal Remediation Technologies Roundtable consisting of representatives from the EPA, Department of the Energy, Department of the Interior, Department of Defense, Department of the Air Force, Department

of the Army, and the Department of the Navy. An on-line version of this report is available at [http://www.frtr.gov/matrix2/top\\_page.html](http://www.frtr.gov/matrix2/top_page.html). The remediation technologies screening matrix identifies processes that have been used to clean up contaminated soil and ground water with some degree of success. The technologies are briefly described, and information is presented to assist in evaluating them for potential application at a site. This review considers only technologies that are applicable to remediation of unsaturated formations contaminated with halogenated VOCs, which is the situation at TA-54.

The evaluation described in this document is based on application of the remediation technologies screening matrix by Van Deuren et al. (1997). Information on the geology and hydrology of the TA-54 MDA L site, on the nature of contaminants and on the extent of the plume was provided to the ITRD and is in the references cited.

### **Review of the Remediation Technologies Screening Matrix**

Van Deuren et al. (1997) identified 14 categories of treatment technologies for soil and ground water remediation. They are:

(For soil, sediment, and sludge:)

- *In situ* biological treatment
- *In situ* physical/chemical treatment
- *In situ* thermal treatment
- *Ex situ* biological treatment (assuming excavation)
- *Ex situ* physical/chemical treatment (assuming excavation)
- *Ex situ* thermal treatment (assuming excavation)
- Containment
- Other treatment processes

(For ground water, surface water, and leachate:)

- *In situ* biological treatment
- *In situ* physical/chemical treatment
- *Ex situ* biological treatment (assuming pumping)
- *Ex situ* physical/chemical treatment (assuming pumping)
- Containment

Air emissions/off-gas treatment

64 technologies were considered in the remediation technologies screening matrix. A brief description of each treatment technology is presented at the beginning of each process description. The information provided for each technology includes the following:

Technology Profile number (refers to Section 4)

Scale status (full scale vs. pilot scale)



Availability  
 Residuals produced  
 Typical treatment train  
 Contaminants treated  
 System reliability/maintainability  
 Cleanup time  
 Overall cost  
 Capital or operation-and-maintenance (O&M) intensive

A brief description of each treatment technology is presented at the beginning of each process description. The technologies applicable to remediation of halogenated VOCs are listed in Table 1. Explanations of the terms in the table are presented in Table 2 and Table 3.

**Table 1. Treatment Technologies Screening Matrix: Treatment of halogenated volatile organic compounds**  
(numbers refer to technologies described by Van Deuren et al., 1997).

Technology	Devel. Status	Use Rating	Applicability	Reliability	Cleanup Time	Function
<b>SOIL, SEDIMENT AND SLUDGE</b>						
<b>3.1 IN SITU BIOLOGICAL TREATMENT</b>						
4.1 Bioventing	Full	Limited	Refer to profile	Refer to profile	Refer to profile	Destruct
4.2 Enhanced Biodegradation	Full	Limited	Better	Refer to profile	Refer to profile	Destruct
4.3 Land Treatment	Full	Limited	Better	Refer to profile	Refer to profile	Destruct
4.4 Natural Attenuation	Full	Limited	Refer to profile	Refer to profile	Worse	Destruct
4.5 Phytoremediation	Pilot	Limited	Average	Average	Worse	Destruct
<b>3.2 IN SITU PHYSICAL/CHEMICAL TREATMENT</b>						
4.6 Electrokinetic	Full	Limited	Average	Average	Average	Destruct
4.8 Soil Flushing	Pilot	Limited	Better	Average	Long	Extract
4.9 Soil Vapor Extraction	Full	Wide	Better	Better	Average	Extract
4.10 Solidification/ Stabilization	Pilot	Limited	Better	Below Average	Average	Extract/ Destruct
<b>3.3 IN SITU THERMAL TREATMENT</b>						
4.11 Thermally Enhanced SVE	Full	Limited	Average	Better	Worse	Extract
<b>3.4 EX SITU BIOLOGICAL TREATMENT (ASSUMING EXCAVATION)</b>						
4.12 Biopiles	Full	Limited	Better	Better	Average	Destruct
4.13 Composting	Full	Limited	Better	Better	Average	Destruct
4.15 Landfarming	Full	Limited	Better	Better	Worse	Destruct
4.16 Slurry Phase Bio. Treatment	Full	Limited	Better	Average	Average	Destruct

Technology	Devel. Status	Use Rating	Applicability	Reliability	Cleanup Time	Function
<b>3.5 EX SITU PHYSICAL/CHEMICAL TREATMENT (ASSUMING EXCAVATION)</b>						
4.17 Chemical Extraction - Solvent Extraction	Full	Limited	Average	Below Average	Worse	Extract/ Destruct
4.18 Chemical Reduction/ Oxidation	Full	Limited	Average	Better	Better	Destruct
4.19 Dehalogenation	Full	Limited	Average	NA	NA	Destruct
4.21 Soil Washing	Full	Limited	Average	Average	Better	Extract
4.22 Soil Vapor Extraction	Full	Limited	Better	Better	Average	Extract
4.23 Solar Detoxification	Pilot	Limited	Better	Average	Average	Destruct
4.24 Solidification/ Stabilization -Vitrification/ Molten Glass	Full	Limited	Average	Better	Short	Extract/ Destruct
<b>3.6 EX SITU THERMAL TREATMENT (ASSUMING EXCAVATION)</b>						
4.26 Incineration	Full	Wide	Better	Average	Better	Destruct
4.28 Pyrolysis	Full	Limited	Average	Inadequate	Better	Destruct
4.29 Thermal Desorption (High & Low)	Full	Wide	Better	Average	Better	Extract
<b>3.8 OTHER TREATMENT</b>						
4.32 Excavation and Off-Site Disp.	NA	Limited	Average	Better	Short	Extract/ Immob.
<b>GROUND WATER, SURFACE WATER AND LEACHATE</b>						
<b>3.9 IN SITU BIOLOGICAL TREATMENT</b>						
4.33 Co-Metabolic Treatment	Pilot	Limited	Refer to profile	Refer to profile	Refer to profile	Destruct
4.34 Enhanced Biodegradation	Full	Limited	Refer to profile	Refer to profile	Refer to profile	Destruct
4.35 Natural Attenuation	Full	Limited	Refer to profile	Refer to profile	Refer to profile	Destruct
4.36 Phytoremediation	Pilot	Limited	Average	Better	Worse	Extract/ Destruct
<b>3.10 IN SITU PHYSICAL/CHEMICAL TREATMENT</b>						
4.38 Air Sparging	Full	Limited	Better	Better	Better	Extract
4.39 Bioslurping	Full	Limited	Average	Average	Average	Destruct
4.41 Dual Phase Extraction	Full	Limited	Better	Average	Average	Extract
4.42 Fluid Vapor Extraction	Full	Limited	Better	Average	Average	Extract
4.43 Hot Water or Steam Flush/Strip	Pilot	Limited	Average	Worse	Better	Extract
4.45 In Well Air Stripping	Pilot	Limited	Better	Better	Average	Extract
4.46 Passive Treatment Walls	Full	Limited	Better	NA	Worse	Destruct
<b>3.11 EX SITU BIOLOGICAL TREATMENT (ASSUMING PUMPING)</b>						
4.47 Bioreactors	Full	Limited	Better	Average	Average	Destruct
<b>3.12 EX SITU PHYSICAL/CHEMICAL TREATMENT (ASSUMING PUMPING)</b>						
4.50 Air Stripping	Full	Wide	Better	Better	Average	Extract
4.51 Liquid Phase Carbon Adsorp.	Full	Wide	Better	Better	Better	Extract
4.54 Separation	Full	Limited	Better	Average	Better	Extract



Technology	Devel. Status	Use Rating	Applicability	Reliability	Cleanup Time	Function
4.56 UV Oxidation	Full	Limited	Better	Worse	NA	Destruct
<b>3.13 CONTAINMENT</b>						
4.57 Deep Well Injection	Full	Wide	Average	Average	NA	Immob.
4.58 Ground Water Pumping	Full	Limited	Average	Better	NA	Extract
4.59 Slurry Walls	Full	Limited	Average	Better	Better	Immob.
<b>AIR EMISSIONS/OFF-GAS</b>						
<b>3.14 AIR EMISSIONS/OFF-GAS</b>						
4.60 Biofiltration	Full	Limited	Refer to profile	Refer to profile	Better	Extract/ Destruct
4.61 High Energy Corona	Pilot	Limited	Better	Worse	NA	Destruct
4.62 Membrane Separation	Pilot	Limited	Better	Worse	NA	Extract
4.63 Oxidation	Full	Wide	Better	Better	NA	Destruct
4.64 Vapor Phase Carbon Adsorp.	Full	Wide	Better	Better	NA	Extract

<sup>b</sup> Presumptive remedy - A presumptive remedy is a technology EPA believes, based on its past experience, generally will be the most appropriate remedy for a specified type of site. EPA established presumptive remedies to accelerate site-specific analysis of remedies by focusing the feasibility study efforts. EPA expects a presumptive remedy, when available, will be used for all Comprehensive Environmental Response Compensation Act (CERCLA) sites except under unusual circumstances.

NA = Not Available.

NOTE: Specific site and contaminant characteristics may limit the applicability and effectiveness of any of the technologies and treatments listed below. This matrix is optimistic in nature and should always be used in conjunction with the referenced text sections, which contain additional information that can be useful in identifying potentially applicable technologies.

**Table 2. Definition of legends used in the treatment technologies screening matrix.**

Factors	Definitions			
<b>Development Status</b> Scale status of an available technology	F Full scale technology has been used in real site remediation		P Pilot Scale: studies conducted in the field or the laboratory to fine tune the design of the technology	
<b>Treatment Train</b> Is the technology only effective as part of the treatment train?	Y Technology must be used with the combination of other technologies as a treatment train		N Technology can be used as a stand alone one.	
<b>Residuals Produced</b> Residuals need to be treated	S Solid	L Liquid	V Vapor	N None
<b>O&amp;M or Capital Intensive</b> Main cost intensive parts	O&M Operations & maintenance intensive	Cap Capital intensive	B Both O&M & capital intensive	N Neither O&M or capital intensive



**Table 3. Definition of criteria used in the treatment technologies screening matrix.**

Factors and Definitions	Worse	Average	Better	Other
Availability Number of vendors that can design, construct, and maintain the technology.	< 2 vendors	2 – 4 vendors	> 4 vendors	NA
Contaminants Treated Contaminants are classified into the following eight groups: - Nonhalogenated VOCs; - Halogenated VOCs; - Nonhalogenated SVOCs; - Halogenated SVOCs; - Fuels; - Inorganics; - Radionuclides; - Explosives.	No expected effectiveness	Either limited effectiveness or nontarget (e.g., VOC treatment by thermally enhanced SVE)	This contaminant group is a treatment target of this technology.	This technology is effective only to certain contaminants, but not all others in the group.
System Reliability /Maintainability The degree of system reliability and level of maintenance required when using the technology.	Low reliability and high maintenance	Average reliability and average maintenance	High reliability and low maintenance	NA
Cleanup Time Time required to clean up a "standard" site using the technology. The "standard" site is assumed to be 20,000 tons (18,200 metric tons) for soils and 1 million gallons (3,785,000 liters) for ground water.	> 3 years for <i>in situ</i> soil	1-3 yr	< 1 yr	Contaminant specific
	> 1 year for <i>ex situ</i> soil	0.5-1 yr	<0.5 yr	Contaminant specific
	> 10 years for water	3-10 years	< 3 years	Contaminant specific
Overall Cost Design, construction, and operations and maintenance (O&M) costs of the core process that defines each technology, exclusive of mobilization, demobilization, and pre- and post-treatment. For <i>ex situ</i> soil, sediment, and sludge technologies, it is assumed that excavation costs average \$55.00/metric ton (\$50/ton). For <i>ex situ</i> ground water technologies, it is assumed that pumping costs average \$0.07/1,000 liters (\$0.25/1,000 gallons).	> \$330/metric ton (>\$300/ton) for soils	\$110-\$330/metric ton (\$100-\$300/ton)	<\$110/metric ton (<\$100/ton)	Contaminant specific
	>\$2.65/1000 L (>\$10/1000 gal) for water	\$0.79-\$2.64/1000 L (\$3-\$10/1000 gal)	<\$0.79/1000 L (<\$3/1000 gal)	Contaminant specific
	>\$11.33/kg (\$25/lb) for air emissions & off gases	\$3.17-\$133/kg (\$7-\$25/lb)	<\$3.17/kg (<\$7/lb)	Contaminant specific

## Application of the Screening Matrix to TA-54

There are several considerations at the TA-54 MDA L disposal area that are particularly relevant in evaluating technologies that may be applicable for remediation. These include:

- Absence of phase separated liquid (free product)
- Large depth to bottom of VOC plume (~100 m or 330 ft)
- Very low organic carbon in tuff resulting in easy desorption of adsorbed VOCs
- Large distance between bottom of VOC plume and underlying aquifer (~200 m or 660 ft)
- The presence of 34 waste disposal shafts, each about 20 m (65 ft) deep, which likely represent a continuing source of contaminants
- The presence of asphalt pavement on much of the site that serves as a cover and LANL would prefer to not move
- High permeability of tuff and corresponding presence of fractures

These conditions are used to evaluate the technologies in the screening matrix.

### *Technologies Eliminated from Consideration*

The fact that contamination is limited to unsaturated formations 200 m (660 ft) above the aquifer eliminates any technology involving ground water (technologies 3.9 through 3.13 in Table 1). The very large depth to the bottom of the plume eliminates any remediation strategy that would require excavation from further consideration. Eliminating excavation is due in part to the costs associated with removing large volume of material, the difficulty and hazards associated with excavating tuff, and the environmental impact that would be incurred by an excavation of this magnitude. These considerations eliminate all *ex situ* remediation options from further consideration (technologies 3.4 through 3.6 in Table 1).

### *In Situ Biological Treatment Technologies*

Van Deuren et al. (1997) identify five *in situ* biological treatment technologies that are applicable to remediation of halogenated VOCs: bioventing, enhanced biodegradation, land treatment, natural attenuation, and phytoremediation. All are based on biological destruction of the contaminants. Their appropriateness for application at TA-54 MDA L is considered below.

**4.1 Bioventing:** Bioventing involves use of injection and extraction wells to deliver oxygen to contaminated unsaturated soils by forced air movement that increases biodegradation of the contaminants by aerobic soil microorganisms. This process is widely used at leaking underground storage tank (LUST) sites to achieve degradation of petroleum hydrocarbons. Because air is used, bioventing is appropriate only for contaminants that degrade under aerobic conditions. It is well established that the more halogenated VOCs such as TCA, TCE and PCE will degrade only under strongly reducing conditions (Rittmann and McCarty, 2001). Therefore, bioventing is not an appropriate technology for remediation of chlorinated VOCs.



4.2 Enhanced Bioremediation: In this process, the activity of naturally occurring microbes is stimulated by circulating water-based solutions through contaminated soils to enhance *in situ* biological degradation of organic contaminants or immobilization of inorganic contaminants. Nutrients, oxygen, or other amendments may be used to enhance bioremediation and contaminant desorption from subsurface materials. Enhanced bioremediation may be used to achieve degradation under either aerobic or anaerobic conditions.

The principal constraint to enhanced bioremediation is that it is based on the ability to circulate water through the contaminated formation; therefore, it is not applicable to contaminants present in the vadose zone. Since the contaminant plume at TA-54 is located in unsaturated tuff, it is therefore not an appropriate remediation technology at this site.

4.3 Land Treatment: Land treatment is used to treat contaminated surface soil in place by tilling to achieve aeration, and if necessary, by addition of amendments. Periodically tilling, to aerate the waste, enhances the biological activity. The contaminants at TA-54 are very deep, hence this technology is not appropriate for application.

4.4 Natural Attenuation in Soils: Natural attenuation relies upon natural processes in soil to reduce contaminant concentrations to acceptable levels. These processes may include dilution, dispersion, volatilization, biodegradation, adsorption, and chemical reactions with soil materials. Natural attenuation may be considered for remediation of contaminants in soils if site-specific factors support its use. The factors include (van Deuren et al, 1997):

- Protection of potential receptors during attenuation
- Favorable geological and geochemical conditions
- Documented reduction of degradable contaminant mass in a reasonable time frame in the surface and subsurface soils
- Confirmation in microcosm studies of contaminant cleanup
- For the persistent or conserved contaminants, ensured containment during and after natural attenuation

Natural attenuation was developed for application at LUST sites in which soil and/or ground water hydrocarbon pollution was noted to persist for many years, yet due to hydrogeologic conditions and the absence of an exposure pathway, there was minimal risk of human exposure to these contaminants. Furthermore, it was observed that in many cases, the size of the contaminant plume actually decreased with time as a result of natural degradation and dilution processes. At sites with very low risk, regulatory agencies have allowed application of this management approach as a way to provide a high degree of protection of health and the environment through relatively modest expenditure of remediation funds.

Natural attenuation is not itself a technology, but rather a management strategy in which the nature and extent of the contaminant plume is determined, potential pathways by which the contaminants might be transported to human receptors or the environment are identified, and then a combination of modeling and monitoring is developed to assure that the risk of exposure is below some acceptable level. Incorporation of modeling in the natural attenuation strategy is important to its success because site managers must convince the regulatory agencies and the public that pollutants will remain below appropriate standards forever and for a variety of future developments. Because the model results are used to



quantify risk assessment, a much higher degree of confidence is needed in the modeling than with other remediation strategies. In some states including New Mexico, ground water regulatory agencies will allow compliance with relaxed alternate ground water standards for selected pollutants at LUST sites at which the risk of exposure is especially low. These alternate standards are established based on the results of a formal risk assessment calculation.

Another factor that is very important in evaluating natural attenuation as a management strategy is incorporation of a monitoring program in the remediation system design. The purpose of the monitoring program is two-fold. First, it will provide data used to validate the models used in the risk assessment. Second, the monitoring program will provide data to confirm that the contaminant plume is behaving as expected and to determine whether contaminants are moving towards a receptor (usually a water supply well).

Use of the natural attenuation management strategy is frequently controversial as it has been characterized as a "do nothing" strategy. In contrast to active remediation methods, it is frequently difficult to convince stakeholders that it is in fact a viable strategy with adequate protection of human health and the environment. Though it has been widely used at LUST sites for hydrocarbon contaminants, the use of natural attenuation for halogenated VOCs has been limited. A DOE site such as LANL will have to include an extensive public participation program to identify its remediation strategy; hence site managers must be able to quantify the risks associated with this option and clearly explain them to the public.

Factors that may limit application of natural attenuation include (Van Deuren et al. 1997):

1. Toxicity of degradation and transformation products may exceed that of the original contaminants.
2. High risks occur at sites where geological characteristics such as fracture bed rock or karst landscapes may prevent assessment of stable plume control for contaminants leached from soil.
3. Contaminants may migrate (erosion, leaching, volatilization) before they are degraded or transformed.
4. Ground water at the site contaminated by the soil source will not be available for an extended period of time.
5. Extensive free product, as nonaqueous phase liquids, may have to be removed before natural attenuation can restore soil in a reasonable time frame.
6. Conservative metals may be only temporarily immobilized with remobilization when natural attenuation reestablishes oxygenated soil conditions.

Only the fifth criterion, the presence of a continuing source of contaminants, appears to be present at TA-54. LANL staff have indicated that a Corrective Measures Study (CMS) for the TA-54 MDA L will eventually be performed, and that this study will evaluate the technical feasibility and risks associated with removing the potential source terms remaining in the waste disposal shafts. However, this study is not expected to be initiated for one to two years. Thus, the magnitude of the source term and the contaminant release characteristics are at present unknown.

Based on the large depth to ground water, the large distance to the nearest water supply well, and the apparent lack of other credible exposure pathways, natural attenuation may be a viable alternative at TA-54. A further consideration is that the extensive modeling done to date can be used to support a risk assessment.

4.5 Phytoremediation: Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment. Contaminants may be either organic or inorganic. The mechanisms of phytoremediation include enhanced rhizosphere biodegradation, phyto-extraction (also called phyto-accumulation), phyto-degradation, and phyto-stabilization. Much of the TA-54 MDA L site is covered with asphalt; hence there is no plant growth. More importantly, most of the contaminants at TA-54 are well below the root zone; hence phytoremediation is not expected to be a viable remediation process at this site.

4.6 Electrokinetic Separation: The Electrokinetic Remediation (ER) process removes metals and organic contaminants from low permeability soil, mud, sludge, and marine dredging. ER uses electrochemical and electrokinetic processes to desorb, and then remove, metals and polar organics. This *in situ* soil processing technology is primarily a separation and removal technique for extracting contaminants from soils. Targeted contaminants include metals, anions, and polar organics. The contaminants at TA-54 are mostly volatile organics of low polarity.

Contaminants in the soil are mobilized through electromigration and/or electroosmosis. Electromigration is movement of ionic constituents as a result of electrostatic attraction to an oppositely charged electrode placed in the soil. Electroosmosis is movement of water due to ionic concentration gradients resulting from electromigration and generally, is a much less important contaminant transport mechanism than electromigration.

Electrokinetic separation is almost certainly not feasible at TA-54 for two primary reasons. First, the contaminants are not electrostatically charged, hence their mobility in an electrostatic field would be due only to electroosmosis, which is very small and requires a large amount of energy. Second, this process requires high water contents in the soil. Van Deuren (1997) report that performance drops off dramatically at moisture contents below 10%. Physical parameters used in LANL's modeling effort consist of gravimetric moisture contents of less than 2% in the Tshirege member (top 41 m or 135 ft) and about 20% in underlying formations.

Electrokinetic separation is in an early stage of development and has seen very limited application at field scale. The contaminants are not those that are readily amenable to mobilization by electrokinetic methods. The site conditions at TA-54 are not well suited for this process. Therefore, it does not appear that electrokinetic separation is an appropriate remediation technology for application at TA-54.

4.8 Soil Flushing: *In situ* soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids must be recovered from the underlying aquifer, and when possible, they are recycled. Because the contaminant plume at TA-54 is in unsaturated tuff at a distance of ~200 m (660 ft) above the water table, soil flushing is not an appropriate technology for application at this site.



4.9 Soil Vapor Extraction: Soil vapor extraction (SVE) is an *in situ* unsaturated zone soil remediation technology in which a vacuum is applied to the formation to induce the controlled flow of air and remove volatile and some semivolatile contaminants from the soil. The gas leaving the soil may be treated to recover or destroy the contaminants, depending on local and state air discharge regulations. Vertical extraction vents are typically used at depths of 1.5 meters (5 feet) or greater and have been successfully applied as deep as 91 m (300 ft). Horizontal extraction vents (installed in trenches or horizontal borings) can be used as warranted by contaminant zone geometry, drill rig access, or other site-specific factors. Soil vapor extraction is widely used to remove volatile petroleum hydrocarbons at LUST sites.

Factors that may limit the effectiveness of SVE include (Van Deuren et al., 1997):

- Soil that has a high percentage of fines and a high degree of saturation will require higher vacuums (increasing costs) and/or hindering the operation of the *in situ* SVE system.
- Large screened intervals are required in extraction wells for soil with highly variable permeabilities or stratification, which otherwise may result in uneven delivery of gas flow from the contaminated regions.
- Soil that has high organic content or is extremely dry has a high sorption capacity of VOCs, which results in reduced removal rates.
- Exhaust air from *in situ* SVE system may require treatment to eliminate possible harm to the public and the environment.
- As a result of off-gas treatment, residual liquids may require treatment/disposal. Spent activated carbon will definitely require regeneration or disposal.
- SVE is not effective in the saturated zone; however, lowering the water table can expose more media to SVE (this may address concerns regarding light non-aqueous-phase liquids [LNAPLs]).

Because of the low organic carbon content of the tuff, halogenated VOCs are not strongly adsorbed to the soil. Furthermore, the low solubility of the contaminants at TA-54 suggests that the bulk of their mass is in the vapor phase. These two factors lead to the expectation that the VOC concentration in the off-gas from an SVE system would be high, and in fact this was confirmed for an abbreviated pilot scale vapor extraction test reported by Neeper (2001). Accordingly, it should be expected that application of SVE at TA-54 will require an off-gas treatment system. While this will add to the cost of remediation, it will also increase public acceptability by ensuring that all contaminants are captured and managed properly.

Based on current knowledge of the site, it would appear that conditions at TA-54 are well suited for application of SVE to achieve remediation. The high volatility and low sorption of the halogenated VOCs at TA-54 suggest that contaminant removal rates by some form of vapor extraction would be very high and that the site could rapidly be remediated by this process.

4.10 Solidification/Stabilization: *In situ* solidification/stabilization (S/S) involves addition of a stabilizing compound such as a cement grout or wax to a contaminated subsurface zone to achieve immobilization of the pollutants. Immobilization may be achieved through both physical and chemical mechanisms. This technology is at a very early stage of development and has been demonstrated at the pilot scale at a limited number of field sites. Its target



contaminant group is inorganics including radionuclides. Conditions at TA-54 that limit application of *in situ* S/S include:

- *In situ* S/S requires drilling wells and injecting the stabilization media to the bottom of the contaminant plume, which is not feasible at MDA L.
- The most common media used for *in situ* S/S are based on cement grouts. This material has limited effectiveness for immobilizing halogenated VOCs.
- Maximum effectiveness of *in situ* S/S requires a high degree of mixing of the stabilization media and the soil. Mixing can be achieved with an auger or through use of high pressure jets to penetrate the surrounding soil. The principal subsurface materials at TA-54 consist of welded tuff that will limit mixing.

A variation of the *in situ* S/S process described by Van Deuren et al. (1997) is the *in situ* vitrification process. In this process electrodes are placed in the ground and sufficiently high current is passed between them that resistive heating melts the soil. Volatile contaminants are either combusted, pyrolyzed, or volatilized and captured by an off-gas collection and treatment system. There are many challenges associated with this process including:

- It is limited to a maximum depth of about 10 m for practical reasons.
- Containment of escaping volatile contaminants is difficult and expensive.
- There are many operational problems that complicate the technology and present appreciable risk to workers.

Based on the large depth of the contaminant plume and the difficulty of stabilizing halogenated VOCs in place, it is apparent that *in situ* S/S is not an appropriate process for application at TA-54.

4.11 Thermally Enhanced Soil Vapor Extraction: Thermally enhanced SVE is similar to conventional SVE but includes the addition of a heat source to increase the volatility of organic contaminants and thus accelerate their removal by vapor extraction. Methods of heating subsurface soils that have been used include electrical resistance heating, application of radio frequency electromagnetic fields and injection of hot air or steam. Except when steam is applied, the heating provides the additional benefit of drying the soil, thereby increasing its permeability, which in turn facilitates passage of air through the formation.

Thermally enhanced SVE is primarily intended to remediate semi-volatile organic compounds such as heavy oils, pesticides, and PCBs. It may also have application to increase the extraction rate of VOCs in soils containing high concentration of natural organic material that, because of its high adsorption capacity, limits their volatility.

Because the contaminants at TA-54 are highly volatile and because there is very little adsorption of these contaminants onto the subsurface soil materials, thermally enhanced SVE does not offer any significant benefit over conventional SVE at this site. Furthermore, because of the large depth and extent of the contaminant plume, it would be difficult and expensive to heat the subsurface soils.

## Summary of the Results of the Screening Analysis

The results of the screening analysis are summarized in Table 4. Only two of the technologies identified by Van Deuren et al.(1997) appear to have application for remediation at TA-54 MDA L: natural attenuation and soil vapor extraction. There are two obvious limitations to natural attenuation. First, the presence of wastes in the 34 waste disposal shafts constitutes a source term for the contaminants that is likely to continue to release pollutants into the formation for many years or decades. Thus, although the extent of the contaminant plume appears to be static based on both modeling efforts (Stauffer et al., 2000) and monitoring results (LANL, 2001a), it is likely that a natural attenuation management strategy would require extensive and costly site monitoring for many decades to assure that the plume did not pose a threat to human health or the environment. The second concern with natural attenuation is that associated with public acceptability. This management strategy is commonly perceived by the public as a “do nothing” alternative and will certainly draw extraordinary scrutiny from citizen activist groups.

Soil vapor extraction is the other process that appears to be feasible for remediation of TA-54. This document constitutes a screening analysis, so details of the process, costs, and duration of remediation activities have not been considered. The preliminary field testing and analyses performed by Neeper (2001) show that large masses of contaminants can readily be removed from deep formations at this site and that air flow through these formations can be easily achieved. Use of atmospheric pumping to achieve air flow through the formation may be feasible at this site. However, an engineering design and economic analysis should be conducted to determine whether the cost savings of no pumping offset the additional costs associated with closer well spacing and longer remediation schedule. A further consideration that needs to be addressed is the design and cost of the off-gas treatment system.

**Table 4. Summary of screening analysis of technologies for remediation of contaminants at TA-54 MDA L**  
(numbers refer to technologies described by Van Deuern et al., 1997)

Technology	Suitability for Application at TA-54 MDA L	Comments
<b>3.1 <i>In situ</i> Biological Treatment</b>		
4.1 Bioventing	Low	<ul style="list-style-type: none"> <li>• Halogenated VOCs are not aerobically degradable</li> </ul>
4.2 Enhanced Biodegradation	Low	<ul style="list-style-type: none"> <li>• Halogenated VOCs are not aerobically degradable</li> </ul>
4.3 Land Treatment	Low	<ul style="list-style-type: none"> <li>• Plume is deeper than can be treated by land application</li> </ul>
4.4 Natural Attenuation	High	<ul style="list-style-type: none"> <li>• Possible because of large depth to ground water &amp; limited exposure pathways</li> <li>• Will require modeling &amp; monitoring for long duration</li> <li>• Questionable public acceptability</li> </ul>
4.5 Phytoremediation	Low	<ul style="list-style-type: none"> <li>• Contaminants deeper than root zone</li> </ul>
<b>3.2 <i>In situ</i> Physical/Chemical Treatment</b>		
4.6 Electrokinetic mobilization	Low	<ul style="list-style-type: none"> <li>• VOCs not mobilized by electrokinetic effects</li> </ul>
4.8 Soil Flushing	Low	<ul style="list-style-type: none"> <li>• Feasibility limited by large distance between bottom of plume &amp; aquifer</li> </ul>
4.9 Soil Vapor Extraction	High	<ul style="list-style-type: none"> <li>• High mobility of VOCs due to volatility &amp; low sorption</li> <li>• High permeability of tuff</li> <li>• Success of limited pilot testing</li> <li>• Off-gas treatment needed</li> </ul>
4.10 <i>In situ</i> Solid./Stab.	Low	<ul style="list-style-type: none"> <li>• Limited by depth of plume</li> <li>• Formation not conducive to grouting</li> </ul>
<b>3.3 <i>In situ</i> Thermal Treatment</b>		
4.11 Thermally Enhanced SVE	Moderate	<ul style="list-style-type: none"> <li>• Enhancement not needed due to volatility &amp; mobility of VOCs</li> </ul>
<b>Technologies Which Are Not Applicable at TA-54</b>		
<b>3.5 <i>Ex situ</i> Biological Treatment</b>		Excavation is not feasible at TA-54
<b>3.6 <i>Ex situ</i> Thermal Treatment</b>		Excavation is not feasible at TA-54
<b>3.9 <i>In situ</i> Biological Treatment</b>		Ground water not contaminated at TA-54
<b>3.10 <i>In situ</i> Physical/Chemical Treatment</b>		Ground water not contaminated at TA-54
<b>3.11 <i>Ex situ</i> Biological Treatment</b>		Ground water not contaminated at TA-54
<b>3.12 <i>Ex situ</i> Physical/Chemical Treatment</b>		Ground water not contaminated at TA-54
<b>3.13 Containment</b>		Ground water not contaminated at TA-54



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- LANL (2001b). Subsurface Vapor-Phase Plumes at Technical Area 54, LA-UR-00-4164, Los Alamos, NM.
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- Van Deuren, Julie, Wang, Zhao, Ledbetter, John, (1997). "Remediation Technologies Screening Matrix and Reference Guide," 3<sup>rd</sup> Ed., U.S. Army Environmental Center, Federal Remediation Technologies Roundtable, Aberdeen Proving Ground, MD. (see also [http://www.frttr.gov/matrix2/top\\_page.html](http://www.frttr.gov/matrix2/top_page.html))

# Attachment to Appendix B

## LANL TA-54 MDA L

### INFORMATION NEEDED FOR DESIGN OF SOIL VAPOR EXTRACTION SYSTEM

#### Introduction

Based on the current understanding of site hydrogeology, including the nature and distribution of contaminants and the hydrologic characteristics of the contaminated formations, the ITRD group conducted an evaluation of remediation technologies that might be appropriate for application at TA-54. This evaluation was done using information and procedures developed by the Federal Remediation Technologies Roundtable consisting of representatives from the EPA, Department of the Energy, Department of the Interior, Department of Defense, Department of the Air Force, Department of the Army, and the Department of the Navy (Van Deuren, 1997). The Roundtable developed a screening matrix that contains 64 remediation technologies that have been developed for cleanup of subsurface contaminated soils, vapors, and ground water. The ITRD group used this screen matrix to determine whether any other technologies, in addition to those considered by LANL, might be appropriate for remediation of the TA-54 MDA L.

The analysis by the ITRD group suggested that two technologies might be appropriate for application at TA-54: monitored natural attenuation and soil vapor extraction. The comparative merits of each process are summarized in Table 1. The uncertainties associated with monitored natural attenuation appear to be much more significant than for SVE, especially the public acceptability of the process. Accordingly, the ITRD group has recommended that LANL conduct a more formal analysis of the SVE process to determine the system design, whether off-gas treatment is needed and how it might be configured, and identify the risks to workers and the public that would be associated with this process.

**Table 1. Summary comparison of monitored natural attenuation and soil vapor extraction for remediation of TA-54 MDA L**

Process	Positive Attributes	Concerns
Monitored Natural Attenuation	<ul style="list-style-type: none"> <li>Reduced remediation costs</li> <li>Limited impact on TA-54 site activities</li> </ul>	<ul style="list-style-type: none"> <li>Public acceptance: It is perceived as "do nothing" approach.</li> <li>May require very long term monitoring</li> <li>Will require risk assessment</li> <li>Poorly quantified source term may complicate process.</li> </ul>
Soil Vapor Extraction	<ul style="list-style-type: none"> <li>Contaminants &amp; site hydrogeology are conducive to efficient SVE remediation.</li> <li>Use of atmospheric pumping may reduce costs.</li> <li>Should achieve rapid remediation</li> </ul>	<ul style="list-style-type: none"> <li>Off-gas treatment may be required.</li> <li>Disruption of TA-54 site activities may occur.</li> <li>May increase risk to workers</li> <li>Poorly quantified source term may complicate process.</li> </ul>

This section identifies the major aspects that would be needed to complete the design of an SVE system that would contain sufficient detail to enable determination of the costs; to compare atmospheric pumping to use of mechanical blowers; to determine potential disruption of TA-54 site operations; and to provide information necessary to conduct an analysis of the risks associated with the remediation activities including both contaminant exposure to workers and the public, and occupational risks to the workers. The recommendations in this section are based on common practice for SVE systems; however, it must be recognized that design of these systems is very site specific. Hence, it is likely that there are other factors that will influence the implementation of this process at LANL.

## **Information Needed for System Design**

There are five major factors that are likely to determine the design of an SVE system at TA-54: 1) site hydrogeologic conditions, including the nature and distribution of the contaminants, and the hydrologic properties of the contaminated formation; 2) the magnitude and characteristics of the source term; 3) the nature of site operational activities which may be affected by the remediation process; 4) regulatory constraints that may be imposed on the site and 5) costs. The discussion in the following sections are presented in the context of two possible variations of the SVE process: an active system based on use of mechanical blowers, and a passive system which removes soil vapors through atmospheric pumping.

It should be recognized that design of any type of soil remediation system is an iterative process that consists of proposing a design, analyzing its effectiveness and costs, and then refining the design. All four factors will influence the design, and it is to be expected that development of an optimal system will require two or more iterations.

## **Site Hydrogeologic Conditions and Contaminant Distribution**

Much of the information needed for the design of an SVE system has already been collected and analyzed by LANL staff through their monitoring programs and in the process of developing a contaminant transport model. The accuracy and completeness of this information has been reviewed by the ITRD team. The well-developed contaminant transport model is of special value in designing an SVE system because it will facilitate evaluation of a variety of extraction alternatives.

Neeper (2001) presented the results of a brief SVE experiment. Data from this test can be used in conjunction with the transport model to estimate the effectiveness of different pumping strategies for contaminant removal. At this point, LANL staff should be able to identify and evaluate the effectiveness of various contaminant extraction alternatives. The effectiveness of each alternative would be considered primarily in terms of contaminant removal rate and the time needed to complete remediation. However, other important factors to be considered include the number, size and depth of wells needed; the air flow rates and pressure drops; the location of the wells relative to surface activities; and the contaminant concentrations in the off-gas and their evolution with time.

**Recommendation 1:** Identify a small number of extraction well configurations, perhaps three alternatives each for an active system and three for an atmospheric pumping system, and use the model to evaluate contaminant removal from the subsurface environment for each of these alternatives.



**Recommendation 2:** Due to the large body of knowledge that has already been collected, additional pump testing of vapor extraction wells is not needed at this site.

### **Characterization of the Source Term**

The wastes that are present in the 34 disposal shafts represent a significant uncertainty for any remediation process because it is not possible to predict what the magnitude of future contaminant release rates might be. While it is possible to do bounding calculations that will predict the effects of a drum burst scenario on soil vapor contaminant concentrations, the number of intact drums, bottles or other containers is not known, nor is it possible to know when or if they will burst.

There are at least four ways in which this uncertainty may be addressed. First, it may be possible to remove the source term. LANL staff have indicated that a future corrective measures study will consider the practicality, the costs, and the risks associated with source term removal. A second possibility may be to stabilize the contaminants in place. This might be done through physical methods such as *in situ* grouting or by using thermal methods such as thermally enhanced vapor extraction. Third, it may be possible to design the SVE system so that it can operate for the foreseeable future if contaminants continue to be detected. For instance, an active system would be designed and operated to remove all of the halogenated VOCs presently in the subsurface environment. Once this is completed, an atmospheric pumping system might be left in place to remove residual contaminants from future drum bursts. Fourth, it may be possible to show that once the existing vapor plume has been removed, natural attenuation becomes a credible method of remediating contaminant releases from future drum burst events. Such an analysis would show that contaminant concentrations and surface release rates would be so low that they did not pose an excessive risk to human health or the environment.

**Recommendation 3:** Perform a corrective measures study to determine the feasibility of removing the waste materials from the disposal shafts or stabilize them in place.

**Recommendation 4:** The remedial system design should include consideration of future drum burst events and provide assurance that contaminant release does not pose an excessive risk to human health and the environment.

### **Nature of Site Operational Activities**

The intention has been conveyed to the ITRD team that TA-54 will continue to remain an operational facility that is integral to waste management activities at LANL for the foreseeable future. These activities have already affected the ability to characterize the site by preventing installation of monitoring wells at some desirable locations. Examples of remediation components that may be constrained by site operational activities include: siting of SVE and monitoring wells, location of SVE pumping and off-gas treatment equipment, and routing of surface piping leading to the vapor extraction (or injection) wells. In addition to the actual components of an SVE system, the installation of monitoring and extraction wells involves use of large equipment such as drill rigs, water trucks, flat bed trucks, and boom trucks. Thus, installation of the wells will result in a large surface disruption for times ranging from many weeks to many months, depending on the number of wells. In addition, the risk to site operations personnel must be considered. This risk may include exposure to

contaminants from the extraction wells as well as usual work place hazards associated with any industrial process.

The impact on site operational activities can be minimized by clearly identifying the nature of these activities and conveying this information to system designers. During the preliminary design phase of an SVE system, the designers will develop a good estimate of the number and location of wells needed for the process, along with the approximate sizes and characteristics of the piping, pumping, and off-gas treatment system. It will then be necessary for managers and remediation system designers to compare the site's operational activities with the SVE system design and collaboratively develop an SVE system design that will achieve remediation having an acceptable impact on TA-54 operations.

**Recommendation 5:** TA-54 site managers should be contacted and asked to identify facility operations that might be impacted by an SVE system. A map of the site should be prepared which delineates structures or areas that cannot have wells, piping or SVE equipment located near them. Areas where site personnel spend large amounts time should also be identified so that the system design can minimize work place hazards.

**Recommendation 6:** Once a preferred SVE option has been determined, TA-54 site managers should review the plan and the construction phasing to be sure that its impact on site operations will be acceptable. As construction progresses, this coordination should be maintained.

## **Regulatory Constraints**

The regulatory constraints that must be met by the remediation system are likely to be important factors in process selection and final design. They must be clearly identified early in the design process, and regulators must continue to be included in discussions involving the remediation system.

Some of the information that system designers need to obtain from regulators include:

- Emission limitations
- Process monitoring requirements
- Site monitoring requirements
- Required cleanup levels
- Long term site monitoring requirements
- Acceptable risk criteria for workers and the public
- Public participation requirements

One of the most important regulatory issues that must be resolved early on is determination of the limitations that may be applied to process emissions, as this will determine whether an off-gas treatment process is required. This limit will likely affect both the concentration of VOCs in the exhaust gas as well as the total mass that may be discharged each day. If the emission limits are not too strict, it may allow use of a slower remediation process such as atmospheric that doesn't require an off-gas treatment process. Slower remediation would involve a trade-off in which a less expensive process is operated for a longer period of time,



in contrast to operation of a more expensive, aggressive SVE system that includes off-gas treatment.

From a regulatory perspective, it is likely that the only process monitoring requirements will be off-gas monitoring. However, it will be necessary to determine what types and frequency of monitoring will be required.

During remediation periodic monitoring of the subsurface contaminant distribution will be required to assess the remediation process and to provide assurance that the contaminant plume is not expanding. The type and frequency of this monitoring must be determined.

The required cleanup level is the residual soil vapor chlorinated VOC concentration that must be met to achieve remediation of the site. The target cleanup levels must be determined. The NMED should clearly identify the cleanup levels and monitoring requirements that LANL must meet in order achieve cleanup of this site. If soil vapor monitoring is to be continued after remediation is complete, the nature, extent and frequency of this monitoring should be identified.

If a risk-based corrective action strategy such as monitored natural attenuation is chosen for application at TA-54, LANL must be informed of the level of risk that is acceptable to the public and to site workers.

A public participation process will be required prior to selection of a final remediation process for this site. NMED and LANL should agree to the nature and scope of this process soon to facilitate development of an effective process and to allow LANL managers to develop an accurate estimate of its cost.

**Recommendation No. 7:** LANL and NMED should continue to work together and identify the regulatory requirements that will affect the design and implementation of the soil vapor remediation process at TA-54. In particular, the following information must be identified: off-gas emission requirements, SVE process monitoring requirements, contaminant plume monitoring requirements, required soil vapor cleanup levels, final monitoring requirements, acceptable public and work risk levels, and public participation requirements.

## **Cost**

The major costs associated with any remediation process can be categorized as either capital costs or operations and maintenance costs. For a soil vapor remediation system, the major capital costs include:

- Drilling and construction of monitoring and extraction wells
- Piping costs associated with connecting extraction wells to the pump system
- Pumping system
- Off-gas treatment system
- Monitoring and control systems
- Civil costs associated with access, utilities, security, etc.

Operations and maintenance (O&M) costs include:



- Personnel costs
- Power costs (electricity, natural gas, water)
- Equipment maintenance
- Process monitoring
- Contaminant plume monitoring

Typical cost estimation practice is to combine the capital costs and the O&M costs to generate an annualized cost. This is done by amortizing the capital costs over the life of the project using an appropriate interest rate that is available to the owner of the process. The annual O&M costs are adjusted for inflation. The two costs are then added to get the annual cost per year. The total cost can be determined by summing the annualized costs over the life of the project. This approach allows direct comparison of systems that have different capital costs, O&M costs, and require different times to achieve remediation.

It is apparent that two general approaches to SVE may be appropriate for this site: an active SVE system that relies upon use of mechanical blowers to circulate air through the formation, and a passive SVE system that relies upon atmospheric pumping for air circulation. Based on the limited pilot work by Neeper (2001), the active system would be expected to move large volumes of air through the formation and have a large radius of influence. Thus, fewer wells would be required and remediation would be accomplished more quickly. However, an active system would require one or more blower systems, an off-gas treatment system, and more extensive piping to connect all of the wells. A passive system relying upon atmospheric pumping would require more wells, less piping, and less or possibly no off-gas treatment, if chlorinated VOC emissions were sufficiently low. The downside of this option is that it would require much longer to achieve cleanup due to the lower contaminant removal rates.

**Recommendation No. 8:** LANL should conduct a design study that includes two variations of the SVE remediation process: one that uses blowers to circulate air through the formation and another that uses atmospheric pumping to circulate air through the formation. Each design should incorporate all of the components needed to comply with regulatory requirements including off-gas emission treatment. The length of time needed to achieve site remediation should be determined for each. The annualized and total costs of each alternative should be determined and used in selection of a final remediation process.

## References

- Neeper, D. (2001). RFI Investigation, presentation to ITRD, Pojoaque, NM, 50 p.
- Van Deuren, Julie, Wang, Zhao, Ledbetter, John, (1997). "Remediation Technologies Screening Matrix and Reference Guide," 3<sup>rd</sup> Ed., U.S. Army Environmental Center, Federal Remediation Technologies Roundtable, Aberdeen Proving Ground, MD. (see also [http://www.fitr.gov/matrix2/top\\_page.html](http://www.fitr.gov/matrix2/top_page.html))

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## **APPENDIX C: COMMENTS AND RESPONSES ABOUT THIS REPORT**

One of the purposes of the ITRD program is to provide an independent evaluation of remediation approaches and applicable technologies on a site-specific basis. The "target audience" for ITRD reports includes both the specific site's Technical Advisory Group, which includes DOE site project managers, M&I/O scientists and engineers, regulators, public stakeholders, and technology experts, and also interested parties with similar challenges at other sites throughout the DOE complex. The intent of the program is to provide technical assistance by developing treatment and deployment information on potentially useful innovative technologies, and to make recommendations in conjunction with all of the parties to a remedial action decision. It has been demonstrated that this inclusive process can help build consensus on a site's eventual technology selection and treatment approach.

Because the ITRD process is inclusive, it seeks to present information to all interested parties in a fair manner. Some of the material and recommendations in this Summary Report for LANL MDA L generated controversy. To capture the discussion about these issues, this appendix contains a series of comments and responses between members of the Technical Advisory Group and LANL Environmental Restoration personnel involved with the project.

Although there were several exchanges of comments and responses, the text of this report includes no changes to the original Technical Advisory Group findings and recommendations from the draft May 2002 reports. However, inclusion of the comments and responses seeks to indicate that there were some areas of dissension that were not resolved within the Technical Advisory Group report.



Comments Topic:		ITRD LANL MDA L TAG Subteam Report: Conceptual Modeling for MDA L, Draft Rev. 2, April 4, 2002		April 25, 2002
#	COMMENT SOURCE	COMMENT	RESPONSE SOURCE	RESPONSE
1.	TAG Subteam Recommendation #1 <i>[see Section 5.1 in the report]</i>	<p><u>Surface emission measurements.</u> The TAG has agreed that the quarterly monitoring at TA 54 MDA L can be relaxed. However, the TAG recommends that additional surface flux measurements be made, preferably by perforating the impermeable cap at some locations. The rationale for this recommendation is as follows:</p> <p>It is being proposed by the Remediation Sub-committee of TAG to use the conceptual model in evaluating and designing remediation alternatives. Before the model can be used for this purpose, it needs to be further validated. Previous validations have compared measured subsurface vapor phase concentrations and surface emissions against model predictions.</p> <p>While the agreement between measured and predicted subsurface concentrations were reasonable, there were significant differences between the corresponding surface fluxes. By perforating the cap, two "data points" can be obtained to further calibrate and/or validate the conceptual model: sampling of the gas phase concentration as well as measurement of the flux.</p> <p>In response to the original TAG report on the conceptual model (Appendix to this report), Don Neeper suggested that CO2 measurements could be correlated to VOC emissions due to barometric pumping. This is a reasonable approach; however, the correlation between CO2 emissions and VOC emissions has to be first demonstrated. A further benefit of surface flux measurements will be in risk evaluation that is being recommended by the two subteams of the TAG.</p> <p>The parameters used in the model to predict the surface emissions (viz. the boundary layer thickness and the diffusion coefficient) need to be re-evaluated (see Recommendation 2 below).</p>	Phil Stauffer, LANL ER	<p>LANL will undertake further analysis of the surface flux enigma during revision of the Modeling document LA-UR 2080.</p> <p>I have implemented Henrys Law with <math>H = 1.5</math> for TCA and the results are interesting. The basic conclusions of the model do not change, however the presence of a dissolved component could affect calculations made in support of remediation.</p> <p>As per Jury et al, alluvium and surface organics may have affected the measurements of TCA surface flux and these effects should be included in any further modeling associated with remediation.</p> <p>Further measurements of surface flux would provide additional data, however at this time there are no plans to do this sampling. This would be a data need written into the remediation work scope.</p>

Comments Topic:		ITRD LANL MDA L TAG Subteam Report: Conceptual Modeling for MDA L, Draft Rev. 2, April 4, 2002		April 25, 2002
#	COMMENT SOURCE	COMMENT	RESPONSE SOURCE	RESPONSE
2.	TAG Subteam Recommendation #2 <i>[see Section 5.1 in the report]</i>	<p><u>Surface flux.</u> The size of the contaminant plume, including whether or not the plume continues to grow or shrinks, is based on a balance between the estimated source of the contaminants and the loss to the atmosphere, or the surface flux. Therefore, the surface flux is a significant factor in the long-term behavior of the plume.</p> <p>The modeled surface flux is based on a porous media diffusion coefficient and a 1-meter transition to a zero concentration in the atmosphere, or boundary layer. This approach is extremely simplified and is not realistic. The boundary layer thickness at the surface is typically 0.5 cm (Jury et al., 1984b), although values can range up to 1 meter for very low wind speeds and stable conditions (Webb et al., 1999). The diffusion coefficient should also be that for open conditions, not for a porous media.</p> <p>The admission that the maximum surface flux from the model is nearly 300 times the maximum values reported from sampling (pg. 23 of Stauffer et al., 2000) is also a concern. Although the differences are rationalized, they should be further evaluated. If the losses are indeed considerably less than predicted by the current model, the growth of the plume will be significantly affected, which may influence the remediation option selected for this site.</p> <p>It is recommended that the surface boundary layer model be changed to be similar to that given by Jury et al., 1984b, and that the simulations be rerun to evaluate the change in surface modeling on the plume behavior. Additionally, data should be collected to support the surface loss component of the model as discussed elsewhere in this report.</p>	Phil Stauffer, LANL ER	<p>The surface flux issue is beyond the scope of the revised LA-UR 2080, however this would be included any modeling performed in support of the remediation alternatives.</p> <p>I have read the Jury documents and agree that the surface flux on any parts of the flat topography (mesa tops) containing alluvium (which contains organics/water) could reduce plume loss to the atmosphere. However, the sides of the mesa generally contain much less alluvium and should continue to be conceptualized as sinks for the VOC vapors.</p> <p>Furthermore, the surface is not blanketed by alluvium and distribution and thickness would need to be measured before using this concept.</p> <p>Finally, the boundary layers reported in Jury et al do not seem appropriate for highly porous, non-soil Bandier Tuff that is actively breathing to the atmosphere. I will continue to look into this topic and will definitely add text to discuss this concept in the revised LA UR 2080.</p>



Comments Topic: ITRD LANL MDA L TAG Subteam Report: Conceptual Modeling for MDA L, Draft Rev. 2, April 4, 2002				April 25, 2002
#	COMMENT SOURCE	COMMENT	RESPONSE SOURCE	RESPONSE
3.	TAG Subteam Recommendation #2 <i>[see Section 5.1 in the report]</i>	<i>Surface flux. [See above]</i>	Dennis Newell, LANL ER	Regarding the surface flux. That study was prior to the new and improved EMFLUX that Beacon Environmental provides (that we used at MDA B and C), and it should really be considered qualitative. To really compare the modeling results to the flux study would require conducting a new flux study. The question is whether or not that is necessary. It is not currently a data need for the RFI. It should also be noted that the surface of the mesa has other heterogeneities like asphalt, trailers, domes, gardens, etc. on and in the vicinity of the source.
4.	TAG Subteam Recommendation #3 <i>[see Section 5.1 in the report]</i>	<u>Presence of Fractures.</u> Some of the units are known to have fractures, yet the conceptual model developed by Stauffer et al., 2000, is a porous media approach without fractures. Because many of the fractures are vertical, they would enhance the vertical migration of the plume and could conceivably increase the calculated migration of the plume.  It is recommended that the effect of fractures on the plume migration be investigated.	Phil Stauffer, LANL ER	Fractures are mainly found in the more welded section of TSH Unit 2. Below this horizon, fractures are much less common and do not generally cut through units. The near surface fractures are often filled with calcite and/or clay. We will include this discussion in the report, with references, however modeling of fractures will have to be done in association with the remediation efforts.



Comments Topic: ITRD LANL MDA L TAG Subteam Report: Conceptual Modeling for MDA L, Draft Rev. 2, April 4, 2002				April 25, 2002
#	COMMENT SOURCE	COMMENT	RESPONSE SOURCE	RESPONSE
5.	<p>TAG Subteam Recommendation #4</p> <p><i>[see Section 5.1 in the report]</i></p>	<p><u>Alternative Methods for Gas Sampling and Analysis at MDA L Site.</u> We recommend acquiring more concentration data at the site using inexpensive but accurate field screening or simple laboratory techniques.</p> <p>To obtain a more accurate conceptual model of the subsurface contamination at the MDA L site, more soil gas measurements are required. Current protocol calls for analysis using Summa Canister collection and contract lab analysis by EPA protocol. This procedure is expensive and not well suited for obtaining a better conceptual understanding of the gas plume at the site. To understand the dynamic behavior that is characteristic of subsurface contaminant gas phase plumes, many inexpensive measurements would be most useful. There are a variety of field and local laboratory (i.e., on site or mobile lab) gas sampling and analysis methods available for deployment. These methods range from standard laboratory methods brought to the field (e.g., gas chromatography/mass spectrometry) to simple detectors sensitive primarily, but not exclusively, to the species of interest (e.g., photoionization detectors, portable acoustic wave sensors, chemiresistors, etc.). Any of these methods may be appropriate depending on the analytes in the gas stream, the detection levels required, the frequency of measurement, etc.</p>	Phil Stauffer, LANL ER	The sampling plan for MDA L is being revisited as part of the TA-54 RFI and these comments will be used to help guide the construction of a more appropriate sampling plan for the VOC plume.

Comments Topic: ITRD LANL MDA L TAG Subteam Report: Conceptual Modeling for MDA L, Draft Rev. 2, April 4, 2002				April 25, 2002
#	COMMENT SOURCE	COMMENT	RESPONSE SOURCE	RESPONSE
6.	TAG Subteam Recommendation #4 <i>[see Section 5.1 in the report]</i>	<u>Alternative Methods for Gas Sampling and Analysis at MDA L Site. [See above]</u>	Dennis Newell, LANL ER	Also regarding ... the utilization of additional screening methods such as a Field GC. Numerous methods were used and evaluated in the past, and the B&K was settled on as the best method. Additionally, we have done some correlations between the B&K TCA and TCE results vs the SUMMA analytical. We are getting linear correlation with an R <sup>2</sup> of ~.90; therefore the B&K is an excellent method for tracking plume behavior (trends), and showing extent; the SUMMAs provide us the "ground truth". With respect to the quantification of TCA and TCE; the B&K appear to read ~70% of the analytical results for TCA, and ~60 % for TCE. A better quantification could be obtained with a two point calibration of the B&K; however, this is much more expensive than a single point calibration (which is what we currently do). If better quantification is really a data need (not in my opinion) then we should spend more on the B&K calibration rather than different methods. It should be possible to address this by documenting a review of all possible methods and their potential application to MDA L environment and data needs. Either one method would be determined best or a comparative study could be recommended.

**Steve Webb** proposed adding the following text at the end of Section 4.1 (Findings) of the TAG report:

Subsequent to these findings, the original model report (Stauffer et al., 2000) was revised (Stauffer, et al., 2002). This revised report addressed many of the concerns in items 1, 4, and 6. Specifically, the revised model considers the following processes not included in the original report. The adequacy of the model revision in resolving the concern is summarized below.

1. Henry's law for dissolved gas (Finding 1e above) - finding resolved.
2. Boundary layer effects (Finding 1a and 6a) - finding not resolved as discussed in the Recommendation section.
3. Gas-Liquid Diffusion Coefficient (Finding 1a and 6a) - finding resolved.
4. Higher source concentrations pre-1985.
5. Fractures (Findings 4 and 6b) - finding not resolved.
6. Gas diffusion model (Finding 1d) - discussion added - no model modifications made - finding not important in present application.
7. Gas-Solid sorption (Finding 1b) - discussion added - no model modifications made - finding not important in present application.

He also proposed adding the following text at the end of Section 5.1 (Recommendations) of the TAG report:

Subsequent to the above original recommendations, the original model report (Stauffer et al., 2000) was revised (Stauffer, et al., 2002) as mentioned earlier. We do not believe that the revised model adequately addresses any of the above recommendations. There has been limited progress on the surface flux issue (Recommendation 2), but much more work remains before the issue is adequately addressed. Therefore, the original recommendations remain unchanged by the revised model report.

**Dennis Newell and Phil Stauffer** (LANL ER) provided the following information: Below are mine and Phil's responses to the TAG conceptual model recommendations and Steve Webb's suggested additions to the report. The report reads as if a great deal of work is recommended, which is contrary to what we have been getting from the conference calls.

#### Section 5.1

[*Recommendations*] 1 and 2. Surface Emission measurements and Surface Flux (we are evaluating these together due to their similarity): Further validation of the model is recommended. Comparison of the model the subsurface concentrations shows that the model is adequate; however surface flux measurement vary significantly from predicted values.

We believe the subteam is assuming that the measure flux values are "correct". In reality, the surface flux will vary with the permeability of the surface. The surface footprint of the plume is very heterogeneous; it is covered with soil, asphalt, base coarse, and has areas of bare, weathered tuff. Additionally, the effective porosity of most of these materials varies due to fluctuating near surface moisture conditions. A "point-in-time"



flux measurement is unlikely to correspond with the predictions. The near surface in the model is greatly simplified.

The team recommends further measurements including penetrating the asphalt cap and taking measurements. We do not understand what that will provide as far as further validation. We have sub-asphalt measurements in the pore gas wells at depths of ~20 ft that agree well with the model. Additional surface flux measurements could be made, but the same surface heterogeneity will impact the agreement with the model. The previous measurements were taken after rain, which will not provide a maximum flux. Measurements would have to be made during dry surface conditions; measurements of the asphalt cap would have to be made.

However, how important are surface flux measurements? We primarily use surface flux to provide a surface expression of the subsurface plume to aid in extent determination. The model fits the subsurface extent. As far as risk assessment of vapors, the surface flux method we used is not accepted; expensive EPA flux chambers would have to be used followed by modeling of the emissions to human receptors. However, for the RFI, SUMMA canister samples of atmosphere at the site were collected to evaluate present day risk, and no such risk was found.

Additionally, surface flux was reduced in the model with the result showing that the goodness of fit becomes poor when surface flux is reduced by even one order of magnitude. Given that the measured surface flux is more than 2 orders of mag. lower than the model predicts, the modeling suggests that surface flux measurements should be used only qualitatively.

*[Recommendation] 3. Presence of Fractures.* The uppermost unit (Unit 2) at MDA L is moderately welded and hosts near vertical fractures. This unit contains the upper ~50 ft of the vapor plume and is in contact with the atmosphere at the surface and mesa sides. One consideration is that the fractures are likely filled to partially filled in the near surface by translocated soils/fill, clay, and carbonates. This would limit vertical movement of vapors through fractures. The geologic unit beneath the uppermost unit is poorly welded and does not host many fractures, and thus any influence of fractures on vapor transport would be insignificant. If the fractures in Unit 2 are included in the model as increased vertical diffusion, much greater loss to the atmosphere would result (which limits the lateral extent of the plume), preventing matching of the model to the data.

Given that the plume is larger than if the upper unit fractures were increasing vapor movement, we do not think additional studies on fractures are warranted. Fracture spacing may need to be included in detailed passive venting studies where fractures could have a profound 'short circuit' effect on vent wells that are open in the Unit 2 interval. The current analysis being reviewed, however, is the model of the site-wide plume.

*[Recommendation] 4. Alternative Methods for Gas Sampling and Analysis at MDA L site.* I have previously provided comments on this topic. The early pore gas monitoring program explored different methods of pore gas detection, including tedlar bags and GCs. The present day methodology has proved to be the most reliable and cost effective method, providing consistent, quality results.

Yes, the B&K results for TCA, TCE, etc can be impacted by the presence of freons. However, we include freon screens in our B&K set-up to compensate for this potential problem. We have not seen a significant problem with interference, except with water vapor at certain times of the year. Over the last few years the correlation between the B&K and associated SUMMA analytical results has been very good, measuring within the expected error in the B&K. The B&K screening has been used primarily to get a very large data set for extent definition. SUMMAs are the ground truth and are used to define nature. Our proposed future monitoring phases out the B&K and moves towards limited SUMMA samples at key locations.

We do not agree with this recommendation and do not think experimentation with additional pore gas methodologies will improve our data set. More likely, it would be costly and take several years of data before an evaluation could be made.

In response to Steve Webb's additional comments:

We state again that the main purposes of the modeling are to show that we have a reasonable understanding of the mechanisms that have created the VOC plume, and that our numerical model of the plume can be used to predict its behavior into the future.

In light of purpose of the model, we disagree with Steve Webb's additional comments. We do not believe that the surface flux issues and the fracture subject are significant enough to warrant additional efforts.

The model has incorporated second order effects, which improve the data/model correlation significantly. We feel that the work performed in support of the ITRD review has shown that the basic modeling was sound, and that the revised model can be used as a starting point for analysis of future plume behavior and remediation options.

We need to consider the scale of the problem. Given the magnitude of the plume (relatively small) and the risk it poses (minimal), we need to ask the question, does the existing model adequately describe the plume for the purposes of proposing and implementing remediation options. We do not need to explore details unless they significantly alter the outcome, with respect to risk to the environment and public. The characterization phase of this project has passed, and we need to move towards a conclusion.

*Steve Webb* responded to the above comments as follows:

1. Surface Flux

If a mechanistic model of the surface flux had been included, such as Jury's model, I might agree with their assessment. However, the current model is not mechanistic and is ad hoc. Because the decrease in the plume size is predominantly due to losses to the atmosphere, I feel this process should be modeled mechanistically and in more detail. It shouldn't be a large effort to include this effect.

2. Fractures

Isn't the Cerros del Rio Basalts formation fractured in places? Inclusion of these fractures could significantly increase vertical migration towards the water table. I seem to recall that there are very few measurements under the plume in this formation - please correct me if I'm wrong.



**Dennis Newell** responded to Steve Webb's comments:

RE: #2. Fractures. Yes, the Cerros del Rio basalts are highly fractured, with other features such as breccia zones and rubble zones, as well as massive, unfractured zones. However, the monitoring near and within the basalts has shown that the plume decreases to detection limit concentrations before the basalt contact. Any vapors entering the basalt are at extremely low, at or below detection limit concentrations. With the extremely high air permeability of the basalt, these are flushed away essentially instantly. The basalt appears to act much like the atmosphere.

As far as the amount of data within the basalt. We have two angle boreholes that penetrate the basalt; they are located directly beneath the two major source areas at MDA L. We have ~5 sample ports in each borehole within the basalt. We have a good data set from these ports, but only sporadic, near detection limit hits, and that is why the data looks sparse.

**Joe Rossabi** had the following comments about the discussion among Dennis Newell and Phil Stauffer (LANL ER) and Steve Webb:

I think we are getting away from the general agreement (from the NM meeting) that the numerical model and conceptual understanding of the site was adequate to move on to the next phase but that there were some things that could be done to improve both the numerical and conceptual models. We're not using the right words that express our agreements, areas for improvement, and perhaps the priority or value of the suggestions for improvement.

Specifically to Dennis and Phil's responses:

I believe the subteam recognizes that the surface flux measurements to date are probably not representative. They are, however, field measured data and are assumed to be reasonably accurate. The issue of disparity between the measurements and the model predictions was not raised as an indictment of the model, it merely indicated an opportunity for better understanding of the system. The suggested additional measurements by quick cutting through the asphalt were an attempt to help resolve the disparity at minimal cost. I believe everyone recognizes that we will be subject to the same heterogeneity issues as were encountered in the previous flux measurements; however, the measurements would add to the data set and may be able to provide a better understanding of the surface flux disparity. The fact that the previous surface flux measurements were made under conditions that may have biased the flux rate low strengthens the argument for additional flux measurements. Although the model may indeed be more representative of how the system is behaving than the point measurements indicate, I think we need to be careful with statements that have the flavor of "the data don't match the model".

The inclusion of fractures might also be a nice addition to the model if the cost for incorporating them is not too great.

Frankly, I like the B&K method and would prefer to use it precisely for the reasons that you all have been using it, i.e., large, very accurate data set. I am familiar with the cross-compensation methods that the B&K folks use to deconvolute overlapping spectra (as



occur with some freons and other VOCs) and have had mixed results in accuracy depending on the amount and type of freon in the soil gas mix when compared with standard GC results. The final arbiter of the use of B&K are the comparisons that you all have made using analytical equipment that is not subject to interference from overlapping spectra (e.g., GC). If the B&K is doing the job, that's good enough for me. With respect to onsite GC (Tedlar bags or whatever) versus Summa and offsite, if the Summas are accurate and more cost effective (or more defensible, would not require costly training or change in protocol, etc.) in comparison to on site GCs or other methods – go for it.

Despite these somewhat long winded responses to responses, I agree that we need to bear in mind the purpose and scope of the model, i.e., to have a reasonable first order understanding of the plume and its behavior to determine the next step in treating or monitoring the plume. Given this, the suggestions for additional work on improving the numerical and conceptual model should be balanced with the activities planned for the next phase of the project. If the value of the additional work is of low priority with respect to other planned activities, then it should be placed in its proper position on the list.

**Michael Smith** provided comments on two sections of text in the report. **Dennis Newell** provided responses to these comments:

[M. Smith]: I'd also like to suggest two small changes to the text.

1. Section 2 (Background Information on MDA L) of the final ITRD report on MDA L contains the following sentence:

The pore gas monitoring provided sufficient data for the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) to estimate the nature and extent of the VOC vapor plume at MDA L.

I don't think NMED has "accepted" or "approved" the estimate. As I recall, NMED wants some more data taken. I'm proposing the following revision to the sentence:

The pore gas monitoring provided data for LANL to estimate the nature and extent of the VOC vapor plume at MDA L as part of the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI).

[D. Newell]: I agree; however if the TAG also feels that N&E can be estimated with some confidence, then it would be useful if the report reflected that.

[M. Smith]:

2. I'm also recommending adding some wording to our Findings under point 7 of Section 4.1. I've typed in the paragraph below with my changes in bold italics.

The model seems to give reasonable answers *when compared to a single field data set*. However, some of the details are open to question, and some additional data or modeling studies are needed. Appendices of the available concentration data would be useful. Confidence in the model would increase through successful comparisons to additional field data sets. The current model can be used to select and implement some remediation field tests and develop general strategies for contaminant control and remediation. The

current model can also be used to focus the next characterization data needs and areas for more refined numerical modeling.

[D. Newell]: It is true that the model is compared to one, representative quarter of data. However, the plume is relatively static, which implies that the model compares well to other quarters. The RFI report for MDA L that is being modified goes into depth on the behavior of the plume over time with respect to both nature and extent. I think this report would be too lengthy to provide that discussion also. Again, the RFI report will provide all the data used to assess the plume.

Also, providing concentration in an appendix does not seem appropriate in this case. The analytical data is provided to NMED in quarterly reports from LANL, and the RFI report will provide the entire data set.

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